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The University of Michigan Ann Arbor, Michigan

DIGITAL COMPUTER ANALYSIS OF CONDENSATION IN HIGHLY EXPANDED FLOWS

Thesis by
Lt. James L. Griffin, USN

In Partial Fulfillment of the Requirements

For the Degree of

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Professional Committee:

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DIGITAL COMPUTER ANALYSIS OF CONDENSATION IN HIGHLY EXPANDED FLOWS

SUMMARY

The application of the IBM 7090 Digital Computer to the theoretical prediction of condensation in highly expanded flows is presented. The equations of the spontaneous nucleation theory of Frenkel (13) are combined with the steady one-dimensional diabatic flow equations for a solution of the expansion of a pure vapor. A digital computer program for the solution of these equations is compiled and presented.

The theoretical prediction of the condensation of nitrogen is compared to experimental results and variations in specific heat, latent heat of vaporization, surface tension, and rate of expansion are investigated. The theoretical calculation is applied to metal vapors and the results for copper and zinc vapors are presented.

The results indicate that the theoretical solution gives a reason—able prediction of the condensation in highly expanded flows. The degree of supersaturation increases with an increased rate of expansion and for a proper set of initial conditions "condensation free" flow is obtainable. The rate of expansion and the surface tension are the most critical parameters in the equations for condensing flow. Variations of specific heat and latent heat of vaporization show only minor effects on the end result.



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TABLE OF SYMBOLS

A nozzle cross-sectional area

A* throat area

B, C saturation curve constants for $\ln p_{\infty} = B - \frac{C}{T}$

C_p specific heat at constant pressure

E energy per molecule

f(n) distribution of n-sized drops

g fraction of the mixture, by mass, which is in the

condensed phase

h enthalpy

J nucleation rate per unit volume

k Boltzmann's gas constant

L latent heat of vaporization

M Mach number

m mass of an atom or molecule

m rate of mass flow

n number of molecules in a liquid drop

N nucleation rate

N_A Avogadro's number

 N_{n} number of n-sized drops

p free stream pressure

 \mathbf{p}_{∞} saturation vapor pressure for a plane surface of liquid

Q heat transferred from the droplet to the vapor

R universal gas constant

r drop radius



LIST OF SYMBOLS (continued)

S drop surface area T temperature Ts surface temperature of the liquid drop t time U velocity Ufg change of internal energy due to condensation specific volume V V volume of one molecule W work of the formation of the droplet station in the nozzle measured from the throat X accommodation coefficient α α n probability that one molecule leaves a unit surface area of a droplet of n molecules β number of molecules striking a surface per unit area per unit time probability that one molecule condenses on a unit surface $\beta_{\rm n}$ - 1 area of a droplet of (n - 1) molecules ratio of specific heats γ fractional deviation from isentropic of the pressure change over increment Δx fractional deviation from isentropic of the temperature ϵ_{T} change over increment Δx molecular weight μ density of the mixture P surface tension σ nozzle diffuser half angle thermodynamic potential φ



LIST OF SYMBOLS (continued)

Subscripts and Superscripts:

()*	refers to droplets of critical size
()	refers to stagnation conditions
() _v	refers to vapor phase
() liq or L	refers to liquid phase
() _{sat}	refers to saturation point
() _i	refers to incremental step in which droplets were originally formed
() _j	refers to incremental step presently being evaluated
() _T	refers to incremental step at temperature T which is being evaluated in the search for onset of condensation
()	refers to an infinite surface of the liquid phase



I. INTRODUCTION AND SURVEY OF THE LITERATURE

The phenomenon of the spontaneous condensation of a gas or vapor into the liquid phase has been the subject of numerous theoretical and experimental investigations for the past three-quarters of a century. The condensation of an expanding vapor was first noted in 1887 by R. von Helmholtz; however, this phenomenon did not enter the field of aeronautics until about 1940 when its occurrence was noted in the supersonic wind tunnel.

In a supersonic nozzle, the gas or vapor undergoes an isentropic expansion which results accordingly in a decrease in the temperature and pressure. Generally the saturation vapor pressure decreases with temperature more rapidly than does the static pressure of the isentropic expansion, hence saturation conditions are approached. If the rate of expansion is very rapid the flow will pass through the point at which saturation temperature and pressure are reached without any condensate being formed. The vapor is then in a non-equilibrium state, supersaturated, in which the existing vapor pressure is higher than the corresponding equilibrium saturation pressure.

The first person to note that a supersaturated vapor can exist was R. von Helmholtz, who showed that saturated steam expanding through an orifice into the atmosphere would remain clear for some distance before becoming cloudy. Stodola (1) furthered this by devising experiments on superheated steam which would detect the onset of condensation and provide evidence of supersaturation.



In the late 1940's and the early 1950's an intensive series of investigations were conducted to determine the condensation of air, water vapor in air, and nitrogen. Many of these were conducted at the California Institute of Technology, and worthy of note are the investigations of Head (2) on water vapor in air, Willmarth and Nagamatsu (3) on nitrogen, and a summary report of GALCIT work by Nagamatsu (4). A series of investigations of air in high speed wind tunnels conducted during this era include the works of Stever and Rathbun (5), Wegener and Reed (6), McLellan (7) and Bogdonoff and Lees (8).

There was a lag of interest in this area in the middle to late 1950's. However, with the advent of the nuclear space propulsion system and the use of metallic vapors as the working fluid for hypersonic wind tunnels, the interest has been renewed. The Office of Naval Research sponsored the recent review of existing theories by Courtney (9) in an effort to stimulate this interest. Many of these theories are built around the spontaneous self-nucleation concept, and they base the collapse of the supersaturated state upon the determination of the rate of droplet growth to the critical drop size. The complexity of the nucleation phenomenon requires that many simplifying assumptions be made in order to evaluate the problem by hand calculations. Courtney (9) attempts to obtain a more complete evaluation of the nucleation theories by carrying out the calculations on a digital computer.

A recent study of air in hypersonic wind tunnels by F. L. Daum (10) indicates that, as yet, there is no proven available theory for predicting the amount of supersaturation expected in a hypersonic nozzle from which may be determined the point of onset of condensation.



Until recently none of the investigations had included the problem of metal vapors. The investigation by Hill, et al, (11) in 1962 adapted the existing theory to the case of metal vapors and provided results which indicate that this is a valid extension of the theory. The development of the nucleation equations and flow equations did not prohibit their application to metals, but since the need had not existed the application was not attempted. The authors noted have not mentioned any adaptation of the digital computer to the hypersonic flow problem. Hill suggests that this is the next logical step and that a computer program should be used to investigate the effect of variations in surface tension, nozzle length, area distribution, inlet conditions, and other parameters as well.

Purpose of the Present Investigation

At the inception of this study there was no known application of condensation theory to the case of metal vapors. The Hypersonic Wind Tunnel Group of The University of Michigan was undertaking the experimental investigation of the condensation of metal vapors in highly expanded flows, and thus arose the need of a method for the theoretical prediction of the onset and magnitude of condensing flow.

Of greater importance was the need for an understanding of the effect a variation in any of the various parameters might have on the end result. Thereby arose the need for a digital computer program from which numerous results can be obtained for multiple combinations of the various parameters.

The extent of the present study is to:

(a) review the literature to determine which of the more promising theories will most readily adapt to the IBM 7090 digital computer,



- (b) write the program and test against some known experimental results to validate the method,
- (c) obtain theoretical results for several metal vapors under reasonable hypersonic test conditions,
- (d) vary surface tension, specific heat, heat of vaporization, and nozzle parameters to show the magnitude of influence on the problem.

The first approach was one toward a general problem with all quantities variable and with multicomponent working fluids. This rapidly exceeded the capabilities of the computer, and of the author, and dictated the simplified approach which is employed. The system will be developed for one-dimensional expansion of pure vapors which obey the perfect gas law and which have a constant ratio of specific heats. Initially the specific heat, latent heat, and surface tension will be taken as constant and later will be varied to observe the effect.



II. THERMODYNAMIC FUNDAMENTALS

A. Isentropic Expansion of a Vapor

The assumption that the vapor follows the perfect gas law is, in general, well justified and the pressure and temperature can be related by

$$\frac{\rho}{\rho_{O}} = \frac{T}{T_{O}}$$
 (2.1)

Any vapor whose latent heat is large, i. e., $L>C_pT$, will approach saturation as the temperature is decreased by an isentropic expansion, and if the expansion is rapid enough there will be a thermal lag so that a supersaturated region will be reached.

The Clausius-Clapeyron equation can be used to relate the variation of the saturation vapor pressure with temperature to the latent heat of vaporization.

$$\frac{\mathrm{dp}_{\infty}}{\mathrm{dT}} = \frac{\mathrm{L(T)}}{(\mathrm{v_{v}} - \mathrm{v_{L}})\mathrm{T}}$$
 (2. 2)

where \textbf{p}_{∞} is the saturation vapor pressure corresponding to a particular temperature and for an infinite droplet radius, L(T) is the latent heat of vaporization, and \textbf{v}_{v} and \textbf{v}_{L} are the specific volumes of the vapor phase and liquid phase, respectively.

Since the liquid occupies a very small portion of the total volume, we will assume v_v - $v_L \doteq v_v$ and $v_v = \frac{1}{\rho_v}$. Assuming L = constant, equation (2. 2) becomes



$$\frac{\mathrm{dp}_{\infty}}{\mathrm{dT}} = \frac{L}{\mathrm{v_v T}} = \frac{\mathrm{p}}{\mathrm{T}^2} \frac{\mathrm{L}\,\mu}{\mathrm{R}} \tag{2.3}$$

where, μ = the molecular weight of the vapor

R = universal gas constant.

In order to compare the slope of the isentrope with (2.3) we will differentiate (2.1) logarithmically,

$$\frac{\mathrm{dp}}{\mathrm{p}} = \frac{\gamma}{\gamma - 1} \frac{\mathrm{dT}}{\mathrm{T}} \tag{2.4}$$

from which,

$$\frac{\mathrm{dp}}{\mathrm{dT}} = \frac{\mathrm{C}_{\mathrm{p}}^{\mu}}{\mathrm{R}} \frac{\mathrm{p}}{\mathrm{T}} \tag{2.5}$$

by virtue of γ = C_p/C_v and R/μ = C_p - C_v . The ratio of slopes is therefore

$$\frac{\mathrm{dp}_{\infty}}{\mathrm{dT}} / \frac{\mathrm{dp}}{\mathrm{dT}} = \frac{L}{C_{\mathrm{p}}T} \quad . \tag{2.6}$$

Thus for the case of $L/T>C_p$ the saturation vapor pressure decreases with decreasing temperature more rapidly than does the vapor pressure in an isentropic expansion, and the supersaturation ratio, p/p_{∞} , continually increases until saturation and, eventually, supersaturation are obtained.

Head (2) gives slope ratios for several vapors and shows a typical value of 2 for nitrogen nozzles operating at normal reservoir conditions. Similarly, he shows that if a vapor had a small latent heat of vaporization, $L/T < C_p$, an isentropic compression is necessary for the approach to saturation conditions.



Upon reaching the saturation point the fluid has a choice of two routes by which to continue the expansion. One, the saturated equilibrium expansion, involves a gradual process of condensation which commences at the saturation point and maintains thermodynamic equilibrium throughout the expansion. The other, a supersaturated expansion, is characterized by a delay in the onset of condensation to some point downstream of the saturation point at which the vapor temperature is well below the corresponding saturation temperature.

Before continuing further with these alternatives it will be necessary to develop the diabatic flow equations which account for the effect of the condensate.

B. One-Dimensional Steady Flow Equations With Condensation

The equations have been derived by many authors; however, we are interested here in a specific case which includes the following assumptions:

- 1. The vapor phase is a pure vapor and may be treated as a perfect gas.
- 2. The condensed mass is a liquid, is uniformly distributed throughout the gaseous components, and has the same speed and temperature as the stream.
- 3. The volume of the condensed phase is negligible compared to the total volume.
- 4. The nozzle flow is frictionless and is without heat transfer.
- 5. The saturation curve for the vapor may be adequately approximated by the Clausius-Clapeyron equation.
- 6. The latent heat of vaporization and the specific heat at constant pressure remain constant.



Assumption 2 requires some discussion, in that the crystallization of the liquid drops or the sublimation directly to the solid state is probable at the lower temperatures. In the area concerned, the available experimental data on the properties of the vapor and the liquid phases is extremely limited, and for the crystalline phase it is practically non-existent. Highly extrapolated curves are the only sources, in many instances, so the liquid assumption will be as good as the available The zero drag approximation is supported by Stever (12) in citing numerous investigations which verify high fractional condensation rates. From the equations of Frenkel (13) it is noted that a small critical drop radius is necessary for a high condensation rate. In high speed flow the drops are in the nozzle for only a short period of time, so there is only time for a small increase in size due to growth. for high speed expansions with supersaturation, the drop size will be small, and the logical assumption is that the condensate and the vapor travel at the same velocity.

Only the major steps in the development of the flow equations for a pure vapor are presented in this section. A more complete development is presented in Wegener (14).

The continuity equation can be written in its usual form, since the volume of the liquid is negligible and the vapor and drops travel at the same velocity. With ρ taken as the density of the mixture and $\mathring{\mathbf{m}}$ as the total mass which passes a given location in unit time:

$$\rho UA = \dot{m} = constant$$

(continuity)
$$\frac{d\rho}{\rho} + \frac{dU}{U} + \frac{dA}{A} = 0$$
 (2.7)

As a result of the assumptions 2 and 3 the equations of momentum and state are:



(momentum)
$$\frac{dp}{\rho} = -UdU$$
 (2.8)

(state)
$$\frac{dp}{p} = \frac{d\rho}{\rho} + \frac{dT}{T} - \frac{dg}{(1 - g)}$$
 (2.9)

From the first law of thermodynamics, with no external heat sources, the energy equation is

$$d(h + U^2/2) = 0$$
. (2.10)

The density of the mixture, ρ , used in the above equations is defined by the equation, $\rho = \rho_V + \rho'_L$. The density ρ'_L is the mass of liquid condensate per unit volume of the vapor. This requires an assumption that the liquid droplets be uniformly distributed throughout the vapor so that the densities of the vapor and of the liquid may be referenced to the same volume. g is the mass fraction of the working fluid which has condensed into the liquid phase.

By use of the assumption that the vapor and the liquid are at the same temperature, and for constant $C_{\rm p}$ and L equation (2.10) becomes,

$$d (U^2/2 + C_pT - gL) = 0$$
 (2.11)

and

(energy)
$$UdU + C_{p}dT - L dg = 0$$
 (2.12)

By introducing the sound speed by the perfect gas formula in terms of vapor density, $A^2 = \gamma \frac{R}{\mu} T$, an alternate form of (2.12) is

$$(\gamma - 1) M^2 \frac{dU}{U} + \frac{dT}{T} - \frac{L dg}{C_p T} = 0$$
 (2.13)



The four equations, (2.7), (2.8), (2.9), and (2.12) involve the six unknowns, p, ρ , T, U, g, and A. For this particular problem, it will be assumed that g and A are determined from other sources and p, ρ , T and U are obtained from the above equations.

Area will be known for a given nozzle, or the area distribution must be determined from a given Mach number or pressure distribution. The question of determining the condensation, g, depends on the assumed flow conditions. If it is assumed that thermodynamic equilibrium exists at all times the Clausius-Clapeyron equation can be used. This method will be developed in Section V. However, in the event supersaturation takes place, the determination of g is not so simple and nucleation theory must provide the missing equation.

After devoting one section to the determination of the onset of condensation, and one to nucleation theory, the flow equations will be married to the condensation equations for a complete solution.



III. PREDICTION OF THE ONSET OF CONDENSATION

A review of the literature shows that indeed there is no proven available theory which is valid for predicting the onset of condensation in a supersaturated flow. A solution of the equations for predicting this point always requires an assumption as to the amount of condensate formed, the droplet formation rate, or the deviation from isentropic flow.

A marriage of the flow equations (thermodynamic) and the condensation equation from nucleation theory provide a means of computing the flow properties for a given area distribution. A plot of a flow parameter during the period of condensation shows a sharp deviation from a plot of the same parameter undergoing isentropic expansion. Experimental investigations have determined that static pressure, p, and pitot pressure, p'o, are strongly affected by condensation and a jump in these quantities usually is used to detect the onset of condensation.

Here we are defining the point of onset of condensation as that point along the flow at which the initial condensate formed is sufficient to cause the computed value of p or T to differ a detectable amount from its corresponding value for the isentropic expansion.

The complete solution could be solved for very small steps starting at the saturation point and continuing throughout the length of the nozzle. From a plot of actual pressure, p, compared to the pressure distribution for an isentropic expansion the point of onset of condensation could be determined. However, this would require an excessive number of calculations, and for certain combinations of nozzle parameters and stagnation conditions the vapor may traverse the nozzle without ever condensing and several minutes of computer time would be wasted.



Therefore, it would seem expedient to establish a criterion for estimating the point of onset of condensation and then to continue the stepwise computation of the full set of equations from this point onward.

Since the expansion of the vapor, in which there is no condensed liquid, will be assumed isentropic, any deviation from isentropic conditions should serve as an indication of condensation. As previously stated, the static pressure is sensitive to condensation and this will be used as an indicator. From the calculations of Hill (11) the static temperature, T, also appears to give a strong indication. At certain times it is quite possible that the temperature might give a better indication than the pressure, and this factor now will be investigated.

The flow equations from thermodynamics, (2.7), (2.8), (2.9), and (2.13), relate isentropic conditions when there is no condensate present, $g = \Delta g = 0$, and relate actual conditions when the vapor is condensing. A proper combination of these equations should produce a parameter which indicates the deviation from the isentrope. Since we are interested in temperature and pressure we will recombine the flow equations to obtain expressions for $\frac{dp}{p}$ and $\frac{dT}{T}$.

$$\frac{\mathrm{d}\rho}{\rho} + \frac{\mathrm{d}U}{U} + \frac{\mathrm{d}A}{A} = 0 \tag{2.7}$$

$$dp = -\rho UdU \tag{2.8}$$

$$\frac{\mathrm{dp}}{\mathrm{p}} = \frac{\mathrm{d}\rho}{\rho} + \frac{\mathrm{dT}}{\mathrm{T}} - \frac{\mathrm{dg}}{1 - \mathrm{g}} \tag{2.9}$$

$$(\gamma - 1) M^2 \frac{dU}{U} + \frac{dT}{T} - \frac{L dg}{C_p T} = 0$$
 (2.13)

Substitute equations (2.7) and (2.13) into (2.9) to obtain



$$\frac{\mathrm{d}p}{p} = -\frac{\mathrm{d}U}{U} - \frac{\mathrm{d}A}{A} - (\gamma - 1) M^2 \frac{\mathrm{d}U}{U} + \frac{L \, \mathrm{d}g}{C_p T} - \frac{\mathrm{d}g}{(1 - g)}$$

$$\frac{\mathrm{d}p}{p} = -\left\langle \frac{\mathrm{d}U}{U} \left[1 + (\gamma - 1) M^2 \right] \right\rangle + \left\langle -\frac{\mathrm{d}A}{A} + \left(\frac{L}{C_p T} - \frac{1}{1 - g} \right) \mathrm{d}g \right\rangle \quad (3.1)$$

from (2.8) and the equation of state, $p = \rho$ (1 - g) $\frac{R}{\mu}T$, we obtain

$$\frac{dU}{U} = -\frac{(1-g)}{\gamma M^2} \frac{dp}{p} .$$

Insert this into equation (4.1) and rearrange

$$\frac{dp}{p} - \frac{dp}{p} \left\{ \frac{(1-g)}{\gamma M^2} \left[1 + (\gamma - 1) M^2 \right] \right\} = \left\{ -\frac{dA}{A} + \left(\frac{L}{C_p T} - \frac{1}{1-g} \right) dg \right\}$$

$$\frac{dp}{p} = \frac{\gamma M^2}{\left[\gamma M^2 - (1-g) - (1-g) (\gamma - 1) M^2 \right]} \left\{ -\frac{dA}{A} + \left[\frac{L}{C_p T} - \frac{1}{1-g} \right] dg \right\}^{(3.2)}$$

For this particular problem we are interested only in the point of onset of condensation. Therefore, we assume isentropic conditions exist up to the point and the only condensate present will be the dg formed over the incremental step at which we are considering the onset to take place. The calculations will be accomplished in a step by step manner on a digital computer, so we write all increments as Δ and set g=0 to get

$$\frac{\Delta p}{p} = \frac{\gamma M^2}{M^2 - 1} \left\{ -\frac{\Delta A}{A} + \left| \frac{L}{C_p T} - 1 \right| \Delta g \right\}$$
 (3. 3)

From (3.3) it can be seen that over steps in which there is no condensate ($\Delta g = 0$) the stepwise change in pressure will be isentropic. However if $\Delta g \neq 0$ then the step change in p will differ from isentropic. We therefore rewrite (3.3) as



$$\frac{\Delta p}{p} = -\frac{\gamma M^2}{M^2 - 1} \frac{\Delta A}{A} \left\{ 1 - \frac{A}{\Delta A} \left(\frac{L}{C_p T} - 1 \right) \Delta g \right\}$$
(3.4)

We now can define

$$\epsilon_{\rm p} = \frac{A}{\Delta A} \left(\frac{L}{C_{\rm p}T} - 1 \right) \Delta g$$
 (3. 5)

as the fractional deviation from isentropic of the pressure change over an increment Δx . The magnitude of ϵ_p which can be considered a significant deviation is yet to be determined.

Now we examine a similar analysis of the temperature as a possible indicator. From equations (2.13) and (2.8) we obtain

$$\frac{dT}{T} = \frac{\gamma - 1}{\gamma} (1 - g) \frac{dp}{p} + \frac{L}{C_p T} dg$$
 (3. 6)

By substituting the value of $\Delta p/p$ from (3. 4) the equation becomes

$$\frac{\Delta T}{T} = \frac{\gamma - 1}{\gamma} \left\{ \frac{\gamma M^2}{M^2 - 1} \frac{\Delta A}{A} \left[- 1 + \frac{A}{\Delta A} \left(\frac{L}{C_p T} - 1 \right) \Delta g \right] \right\} + \frac{L}{C_p T} \Delta g$$

$$\frac{\Delta T}{T} = \frac{(\gamma - 1) M^2}{M^2 - 1} \frac{\Delta A}{A} \left\{ - 1 + \frac{A}{\Delta A} \left[\left(\frac{L}{C_p T} - 1 \right) + \frac{M^2 - 1}{(\gamma - 1) M^2} \frac{L}{C_p T} \right] \Delta g \right\}$$

$$\frac{\Delta T}{T} = -\frac{(\gamma - 1) M^2}{M^2 - 1} \frac{\Delta A}{A} \left\{ 1 - \frac{A}{\Delta A} \left[- 1 + \frac{L}{C_p T} \left(\frac{\gamma - 1/M^2}{\gamma - 1} \right) \right] \Delta g \right\} \tag{3.7}$$

Again we define

$$\epsilon_{\mathbf{T}} = \frac{\mathbf{A}}{\Delta \mathbf{A}} \left[\left(\frac{\gamma - 1/\mathbf{M}^2}{\gamma - 1} \right) \frac{\mathbf{L}}{\mathbf{C}_{\mathbf{p}} \mathbf{T}} - 1 \right] \Delta \mathbf{g}$$
 (3.8)

as the fractional deviation from isentropic of the temperature change over Δx .



Note: A comparison of (3.5) and (3.8) shows a difference only of the coefficient of L/C_pT . Thus as $\left(\frac{\gamma-1/M^2}{\gamma-1}\right)-1$, i.e., as $M\to 1$, ϵ_T approaches the value of ϵ_p . However, an examination of ϵ_T and ϵ_p for given conditions of L/C_pT , ΔA , Δg produces:

- (a) for condensation in the supersonic portion (M > 1) $\epsilon_{
 m T} > \epsilon_{
 m p}$
- (b) for condensation in the subsonic portion (M < 1) $\epsilon_{
 m p} > \epsilon_{
 m T^{\circ}}$

As an example we consider reasonable values of L/C $_p$ T = 3 and M = 10: the result gives ϵ_p = (2) $\frac{A}{\Delta A}\Delta g$ and ϵ_T $\stackrel{\text{\tiny a}}{=}$ (9.5) $\frac{A}{\Delta A}\Delta g$. Therefore, a dual criteria will be selected so that ϵ_T will determine the onset of condensation when M > 1 and ϵ_p will be used when M < 1.



IV. NUCLEATION THEORY

A. Condensation Nuclei

In the process of condensation, the saturated state is referenced to a plane liquid phase and the vapor is considered to condense on a flat liquid surface or on a "cold" container wall such as the moisture formed on the outside surface of a glass of ice water. However, in highly expanded flows the liquid surface is not present and the "cold" wall is not available, due either to the "hot" boundary layer surrounding the flow in a nozzle or to the total absence of a wall in the case of the free jet.

These surfaces appear either in the form of impurities, such as particles of dust, etc., or as small drops formed of clusters of molecules of the vapor itself united by statistical collision.

Obviously, for a truly pure vapor there would be no foreign nuclei; however, dust particles in clean air have been estimated upward of 10^3 particles per cubic centimeter, so this possibility must be considered. Head (2) has shown that these foreign nuclei do play an important role in the onset of condensation. However, for highly expanded flows where the stay time is very short, Stever (12) has shown that the high rate of condensation could not be caused by condensation onto the foreign nuclei alone. Stever (12) quotes an example from Oswatitsch's study of water vapor which considers 10^5 foreign nuclei per cubic centimeter traveling in a gas for a distance of 10 centimeters where there is super cooling of 30° C. A slightly supersonic velocity of 3. 3 x 10^{4} centimeters per second would traverse this 10 centimeters in 3 x 10^{-4} seconds. Using the faster growth formula for droplet growth gives a



radius of growth of about 3×10^{-5} centimeters in this distance. The amount of water condensed over this span then is 10^{-8} grams per cubic centimeter, which releases an amount of heat that is very slight and which has an insignificant effect on the flow quantities. The actual condensation process has a marked effect upon the flow properties; therefore it must be concluded that the number of drops far exceeds the number of foreign nuclei. We must then resort to the spontaneous formation of the droplets onto which condensate growth occurs.

There is an opening in the above argument, in that the growth rate onto the foreign nuclei could be grossly in error. However, Head (2) found droplet formation rates on the order of 10^{16} drops per cubic centimeter per second in his investigation of water vapor; thus, the high particle formation rate tends to support Stever's argument.

For this analysis it will be assumed that the condensation phenomenon is one of spontaneously formed nuclei and is triggered by the attainment of critical size droplets onto which the supersaturated vapor condenses.

The concept of the critical drop size as developed in Stever (12) stems from the energy required to evaporate a drop of liquid which contains n molecules.

$$E(n) = n E_{\infty} - 4\pi r^2 \sigma \qquad (4.1)$$

In (4.1) E_{∞} is the energy required to remove by evaporation a single molecule from an infinite surface of liquid and σ is the surface tension. To evaporate one molecule would require

$$\Delta E(n) = E_{\infty} - \frac{2\sigma V_{liq}}{r}$$
 (4. 2)



where V_{liq} is the volume of a molecule of the liquid. An application of Boltzmann's law gives vapor pressure

$$p = K \cdot e^{-\frac{\Delta E}{k T}}$$

and the equilibrium vapor pressure for a plane surface

$$p_{\infty} = K \cdot e^{-\frac{E_{\infty}}{kT}}$$

Combining these gives the Thompson-Gibbs equation

$$\frac{p}{p_{\infty}} = e^{2V_{\text{liq}}\sigma/rkT}$$
 (4.3)

Expressing the molecular volume V_{liq} as $\mu/N_A\rho_L$ and rewriting it as a log function, (4.3) becomes

$$\ln p/p_{\infty} = \frac{2\mu\sigma}{r\rho_{\perp}kN_{A}T} = \frac{2\mu\sigma}{r\rho_{\perp}RT}$$
 (4. 4)

Note that with the occurrence of r in the denominator of equation (4. 4) the equilibrium between the vapor and the liquid drop is unstable. For a vapor which is saturated with respect to a given drop size, if one molecule sticks to the drop the radius increases and the existing vapor pressure is greater than the new equilibrium vapor pressure; thus, condensation will continue. The reverse is true for evaporation, in that if one molecule evaporates the existing pressure is lower than equilibrium and evaporation continues.

Thus arises the concept of the critical drop radius, r^* , for which $r < r^*$ the droplet vaporizes and for $r > r^*$ the droplet grows. Solving (4.4) gives



$$r^* = \frac{2\mu\sigma}{\rho_L RT \ln p/p_{\infty}}$$
 (4. 5)

Hill (11) points out that in a constant environment, if the critical radius was used to specify the initial drop size then the growth rate would be zero and there would be no condensation because at critical size the decay and growth are equally probable. Hill bases his use of 1.3 times the critical radius on Becker and Doering's conclusion that at that size the probability of decay is close to zero. In this analysis the vapor will be flowing and any critical drops formed will not remain in a constant environment very long since the quasi-steady steps for the calculations will be very small. Therefore, the commonly used r* of equation (4.5) will be used as the initial drop size.

B. Kinetics of Nucleation and Condensation

As implied previously, the spontaneous nucleation approach will be the only one considered in this analysis. There have been volumes written in the development of this area and no attempt at reproduction will be made here. The general approach and final result of the most frequently referenced authors will be stated, however.

In highly expanded flows the state of the vapor can change very rapidly from the unsaturated state to the highly supersaturated state. Frenkel (13) treats the equilibrium distribution of drops in an unsaturated state as a dilute solution of different substances in the vapor as a solvent. By classifying the different solutes by the number of molecules, n, they have in a drop, he obtained the expression for the number of drops containing n molecules.

$$N_{n} = N_{v} e^{-\frac{1}{kT} \left[(\phi_{liq} - \phi_{v}) n - 4\pi r^{2} \sigma \right]}$$
(4. 6)



where N_v = number of molecules in the vapor state ϕ_{liq} , ϕ_v = thermodynamic potential of single molecule $4\pi r^2 \sigma$ = surface energy term.

This droplet distribution is based on the assumption of equilibrium $(\phi_{\rm v}<\phi_{\rm liq})$; however, it is generally assumed that the same distribution can be used for supersaturated conditions $(\phi_{\rm liq}<\phi_{\rm v})$. Note that for the supersaturated condition the number of drops increases with increasing radius and the distribution is unstable. Thus, it becomes essential to determine the rate at which the distribution changes from the stable distribution of the unsaturated state to the unstable distribution of the supersaturated state.

This requires a determination of the rate of formation of critical sized drops, J, in drops per cubic centimeter per second.

Head (2) states the equilibrium equation of Volmer

$$J = K \cdot e^{-\frac{\Delta W}{kT}} = K \cdot e^{-\frac{4\pi r^{*2}\sigma}{3kT}}$$
(4.7)

where ΔW is the total work of the formation of the droplet.

The determination of the constant, K, has been developed by several authors, including Volmer, Becker and Doring, and Frenkel.

All assume a quasi-stationary phase transition process in which the number of molecules which condense are instantly replaced in the vapor such that the number of vapor molecules is maintained constant.

Volmer considered only the number of drops reaching critical size, the number of vapor molecules striking the surface of the critical size drop per unit time, and the number of molecules in a drop of critical size.



Becker and Doring derive the nuclei formation frequency purely from kinetic considerations and take into account the evaporation from the surface of the drop, as well as the condensation onto it. This approach is considered by most authors to be better than others; however their solution is rather difficult to apply.

Frenkel uses the method of Zeldovich to integrate the differential equations of Becker and Doring and gets a much simpler derivation of an equation that is almost identical to that of Becker and Doring. The ratio of the result of Frenkel to that of Becker-Doring is $(n^*)^{2/3}$ and this is considered minor. n^* is the number of molecules in a critical sized drop.

A partial derivation of the nucleation rate equation is presented in Appendix A. This derivation is necessitated by an apparent error of π in the original equation presented by Frenkel (13).

For this analysis, equation (A. 7) will be applied as the nucleation rate equation.

$$J = \left(\frac{p}{kT}\right)^{2} \frac{1}{\rho_{L}} \sqrt{\frac{2\mu\sigma}{\pi N_{A}}} e^{-\frac{4\pi\sigma r^{*2}}{3kT}}$$
(4.8)

where J = number of critical drops formed per unit volume per unit time.

C. Limitations

1. Generally σ as a function of temperature is not known and this is a large factor in the result. Surface tension appears to the third power in the exponent; hence a small error will have a large effect upon J.



- 2. The rapidity of expansion will show marked deviations from the assumed quasi-stationary condition.
- 3. The condensing flow may have sublimation directly from vapor to solid which is not considered.
- 4. At high degrees of supersaturation the drop radius will be small, and Head (2) has shown that the variation of σ with r is large for drops of few molecules. Stever and Rathbun (5) have included this effect into the Frenkel equation to obtain

$$J = \frac{p V_{liq}}{(kT)^2} \sqrt{\frac{2}{\pi m}} \sqrt{\sigma (r^*) - r^* \left(\frac{\partial \sigma}{\partial r}\right)_{r^*}} e^{-\frac{8\pi}{kT} \left(\int_{0}^{r^*} r \sigma dr - \frac{1}{3} r^{*2}\right)}$$
(4.9)

Bogdonoff and Lees (8) have an approach which is entirely different from that of Head and Stever and which produces quite different results. Until these theories have been developed further, it is not practical to include either theorem in this analysis.

From the previous discussion of the assumptions made in the formulation of the nucleation theory and of the limitations above, it is apparent that the best one can expect in an analysis such as this will be an order of magnitude estimate of the condensation parameters and a qualitative analysis of the flow conditions.

D. Growth Estimates

Heretofore, in order to calculate the formation of the critical drops, we have considered the temperature of the liquid drops to be the same as the surrounding vapor. In actuality, the impinging and vaporizing of



molecules onto and away from the droplet leave a surface temperature that approaches the saturated equilibrium value for the surrounding vapor. This temperature difference allows for growth of the particle. The growth of small drops, i. e., r << mean free path, occurs by the molecular transport of molecules onto the surface, some of which condense, and by the conduction away of latent heat of vaporization by the evaporation of a fewer number of molecules which leave at higher kinetic energies.

Oswatitsch laid the basic groundwork for growth in a flowing vapor. Stever (12) follows the method of Oswatitsch to develop an equation for the growth rate of the small drop.

The development presented by Stever makes use of the kinetic theory of free molecule flow (See Patterson (15)). Consider a drop of radius r, temperature T_{liq} , and saturation pressure $(ps_{\infty})_{liq}$ with a surrounding vapor of pressure p and temperature T. The heat transfer from drop to vapor per unit time is

$$Q = \sqrt{\frac{2}{\pi}} p \sqrt{\frac{k}{mT}} (T_{liq} - T) \alpha$$

where α is an accommodation coefficient which varies from 0 to 1, depending on the vapor and liquid surface.

Also from kinetic theory the heat transferred to the drop surface due to condensation is Lfp $\sqrt{kT/2\pi}$ m where p $\sqrt{kT/2\pi}$ m is the amount of vapor (in the form of molecules) impinging on a unit surface and f is the fraction which condenses. The energy being transferred to the surface is equated to the energy being transported away to obtain an expression for f;



$$f = \frac{2\alpha (T_{liq} - T)}{LT}$$

the mass $M_{\overline{D}}$ of the drop is then increased by

$$\frac{\mathrm{d}\, M_D}{\mathrm{d}t} = \frac{1}{L} \, 4\pi \, \mathrm{r}^2 \sqrt{\frac{2}{\pi}} \, \alpha \, \mathrm{p} \, \sqrt{\frac{\mathrm{k}}{\mathrm{mT}}} \, (\mathrm{T_{liq}} - \mathrm{T}) \quad .$$
 Since
$$M_D = \frac{4}{3} \, \pi \, \mathrm{r}^3 \, \rho_L \qquad \text{and} \qquad \mathrm{d}\, M_D = 4\pi \, \mathrm{r}^2 \, \rho_L \, \mathrm{dr},$$

$$\frac{\mathrm{dr}}{\mathrm{d}t} = \sqrt{\frac{2}{\pi}} \, \frac{\alpha}{L} \, \frac{\mathrm{p}}{\rho_L} \, \sqrt{\frac{\mathrm{k}}{\mathrm{mT}}} \, (\mathrm{T_{liq}} - \mathrm{T}) \quad .$$

If the calculation is made in quasi-steady steps, time can be expressed as a function of step length and

$$\Delta r = \sqrt{\frac{2}{\pi}} \frac{\alpha}{L} \frac{p}{\rho_L} \sqrt{\frac{k}{mT}} (T_{liq} - T) \frac{\Delta x}{U}$$
 (4.10)

where the accommodation coefficient, α , is a constant, approximately equal to 1 and T_{lig} is the temperature of the surface of the liquid drop.

The accommodation coefficient α is expressed by Kennard (16) as

$$\alpha (\mathbf{E_i} - \mathbf{E_w}) = (\mathbf{E_i} - \mathbf{E_r})$$

where $E_i = E$ nergy brought up to a unit area per unit time by the impinging molecules

E_r = Energy carried away from the molecules leaving a
 unit surface per unit time

E_w = Energy that the departing molecules would carry away if they carried away the same mean energy per molecule as does a stream issuing from a gas in equilibrium at the surface temperature.



Patterson (15) lists coefficients of the range from . 8 to 1.0, and Stalder (17) found that for free molecule flow an accommodation coefficient of 0.9 checks well with test results. Thus we arrive at the statement, "approximately equal to 1." This only applies for cases where free molecule flow can be assumed to prevail.

On the other hand, where r approaches the magnitude of the mean free path the heat removal is controlled by normal gaseous heat conduction. For this large drop Stever (12) gives the growth equation for period of time, t,

$$\Delta r = \sqrt{\frac{2k (T_{\text{liq}} - T)}{L \rho_L}} t . \qquad (4.11)$$

Other authors have made similar analyses, and Wegener (14) records the quasi-steady solution of Buhler (18) which includes an expression for the condensation coefficient.

$$\frac{\mathrm{dr}}{\mathrm{dx}} = \frac{\mathrm{C}_{\mathrm{p}}}{\mathrm{L}} \frac{\rho_{\mathrm{v}}}{\rho_{\mathrm{L}}} \frac{1}{\mathrm{M}} \left(\frac{1}{2\pi\gamma} \right)^{\frac{1}{2}} \frac{(\mathrm{T}_{\mathrm{s}} - \mathrm{T})}{\left(1 - \frac{2\sigma}{\mathrm{r}\rho_{\mathrm{L}} \mathrm{L}} \right)}$$
(4. 12)

where T_s , the surface temperature of the drop, may be chosen as the equilibrium saturation temperature of the vapor with respect to the drop. As in the previous case, Wegener states (4.12) is valid only for small drops and the equation recommended for large drops is merely a revised form of (4.11).

Hill (11) notes that typical calculations of condensation nuclei indicate very small sizes which are generally much smaller than the mean free paths; thus only the free molecule equations need be considered.



His analysis produces a growth rate expression of

$$\frac{\mathrm{dr}}{\mathrm{dt}} = \frac{3p}{2U_{\mathrm{fg}} \rho_{\mathrm{L}} \sqrt{2\pi RT}} \left[RT_{\mathrm{D}} - RT \right]$$
 (4. 13)

in which $U_{fg}=$ change of internal energy due to condensation. The term T_D is droplet temperature, and Hill presents calculations to show that the rate of drop temperature change is enormous compared to the rate of growth. For water vapor the temperature approaches wet bulb temperature in approximately the same time that it takes the number of molecules in the drop to increase by a factor of 10. Hill uses this in expanation of the assumption used by Oswatitsch that the drops always have wet bulb temperature during the growth period.

After a displacement, the drop temperature will rapidly approach the temperature at which d $T_D/dt=0$ at a much greater rate of change than dr/dt. Hill uses this to form an expression for T_D which depends only upon the instantaneous values of r, p and T.

$$\frac{2}{3} \frac{U_{fg} \xi}{RT} \left\langle 1 - \frac{p_{\infty}}{p} \exp \left[\frac{2\sigma}{\rho_{L} RT_{D} r} \right] \sqrt{\frac{T}{T_{D}}} \right\rangle = \frac{T_{D}}{T} - 1$$
 (4.14)

where ξ is the fraction of impinging molecules which condense.

From the investigations on water vapor, nitrogen, air and a few metal vapors it appears that for highly expanded flows the small drop size is the general rule. The calculations will then be initiated by applying (4.10) as the growth rate equation and choosing drop temperature as the equilibrium saturation temperature of the vapor. The accommodation coefficient in (4.10) will be varied to study the effect and α will be placed into the computer program as a data input so that accurate values, when known, can be used for the calculation.



V. ANALYSIS

The basic equations are established in Sections II through IV. The proper combination of these equations produces a theoretical solution for the hypersonic expansion of a pure vapor in which a supersaturated state occurs. Another solution is obtained for which there is saturated equilibrium expansion in lieu of the supersaturated portion. Both solutions, however, stem from the same basic model.

The basic model considered here consists of assuming:

- 1. "One-dimensional nozzle" with geometrically specified inlet and diffuser.
- 2. A pure vapor with specified stagnation conditions and known: constant specific heats, latent heat of vaporization; surface tension, for infinite radius as a function of temperature; and saturation curve.
- 3. An isentropic expansion to the point of onset of condensation and then diabatic flow through the region in which condensation is taking place.

A. Basic Assumptions

In addition to the assumptions of the basic model, this analysis also embodies the multitude of simplifying assumptions which have been included in the derivation of the basic equations. The type of equations and the specific assumptions made are:

1. Flow equations

- a. Mass flow is constant
- b. Flow is one-dimensional and steady state
- c. Volume of condensed phase is negligible when compared to the total volume



- d. Nozzle is frictionless with no heat transfer across nozzle wall.
- e. Condensed mass is liquid, is uniformly distributed throughout the gaseous components, and has same speed and temperature as the stream
- 2. Prediction of onset of condensation equations
 - a. This embodies same assumptions as flow equations
 - b. No condensate is formed prior to the predicted point of onset of condensation
- 3. Nucleation equations
 - a. Drops are formed by spontaneous nucleation only
 - b. Only drops reaching critical drop size continue to grow
 - c. Number of molecules of vapor is maintained constant
 - d. Saturation pressure corresponds to saturation pressure of a droplet of infinite radius
 - e. The ordered velocity of the particles is neglected
 - f. Equilibrium values of the probabilities that one molecule will leave from or condense on a unit surface and equilibrium particle distributions are assumed valid for the non-equilibrium case
- 4. Growth rate equations
 - a. Drop radius is much less than mean free path
 - b. Accommodation coefficient, α , is approximately equal to 1.0
 - c. Drop temperature is assumed equal to the saturation temperature that corresponds to the pressure of the vapor



B. Supersaturated Expansion

The supersaturated expansion passes the saturation point without any condensate being formed; therefore, a four step solution is required:

1. Isentropic equations from Shapiro (19) and NACA Report 1135, are used to calculate the expansion of the vapor to the point of condensation.

$$p = p_O \left(\frac{T}{T_O} \right)^{\frac{\gamma}{\gamma - 1}}$$
 (5. 1)

$$\mathbf{M} = \left[\frac{2}{\gamma - 1} \left(\frac{\mathbf{T}_{O}}{\mathbf{T}} - 1 \right) \right]^{\frac{1}{2}}$$
 (5. 2)

$$\rho = \rho_0 \left[1 + \frac{\gamma - 1}{2} M^2 \right]^{-\frac{1}{\gamma - 1}}$$
 (5. 3)

$$A = \frac{A^*}{M} \left[\frac{2}{\gamma + 1} \left[1 + \frac{\gamma - 1}{2} M^2 \right] \right]^{\frac{\gamma + 1}{2(\gamma - 1)}}$$
 (5. 4)

$$U = [2 C_{p} (T_{o} - T)]^{\frac{1}{2}}$$
 (5. 5)

At any particular value of T the above equations are readily evaluated for given p_0 , T_0 , ρ_0 , γ , C_p and A*. The station at which these values apply is then determined from the given nozzle geometry?

2. The saturation point is established by an iterative balance of the saturation curve equation with the isentropic flow equation.



The saturation curve can generally be expressed in the form $\ln p_{\infty} = B - \frac{C}{T}$, in which B and C are constants whose value depend upon the choice of units for p and T. The equations which require joint solution are

$$T_{sat} = \frac{C}{B - \ln p_{sat}}$$
 (5. 6)

$$p_{sat} = p_{o} \left(\frac{T_{sat}}{T_{o}}\right)^{\frac{\gamma}{\gamma} - 1}$$
 (5.7)

The isentropic relations above are then utilized to calculate M_{sat} , P_{sat} , T_{sat} , A_{sat} , ρ_{sat} , and U_{sat} .

3. The point of onset of condensation is determined by taking steps, ΔT, of supersaturation and computing the flow parameters from the isentropic relations for each successive step. The isentropic values of each incremental step in temperature are introduced into the nucleation equations for critical drop size and formation rate.

$$r^*_{T} = \frac{2\mu\sigma}{\rho_{L} RT \ln p/p_{co}}$$
 (4. 5)

$$J_{\mathbf{T}} = \left(\frac{p}{k\mathbf{T}}\right)^{2} \frac{1}{\rho_{\mathbf{L}}} \sqrt{\frac{2\sigma\mu}{\pi N_{\mathbf{A}}}} e^{-\frac{4\pi \sigma r^{*2}}{3k\mathbf{T}}}$$
(4. 8)

Note that choice of a very small ΔT will cause the first step to remain very near the saturation point and the resultant $p/p_{\infty} \doteq 1$ will cause r* to approach an infinite radius. r* falls off very rapidly, however, as the degree of supersaturation increases, and for most cases a choice of $\Delta T \geq 5^{O}$ k is sufficient.



The growth rate is zero for the critical droplet at the instant of formation; therefore the nucleation rate for this increment is

$$N_T \approx J_T A_T \Delta x_T$$
 (5.8)

The mass fraction of condensate formed in this increment is

$$\Delta g_{\mathbf{T}} = \frac{4\pi\rho_{\mathbf{L}}}{3\dot{\mathbf{m}}} \dot{\mathbf{N}}_{\mathbf{T}} \mathbf{r}^*_{\mathbf{T}}^3 \tag{5.9}$$

The epsilon equations from the onset of condensation development, (3.5) and (3.8), are now used to determine if this amount of condensate is sufficient to cause an appreciable deviation from the isentropic expansion.

$$\epsilon_{\rm p} = \frac{A}{\Delta A} \left(\frac{L}{C_{\rm p}T} - 1 \right) \Delta g$$
 (3. 5)

$$\epsilon_{\mathbf{T}} = \frac{A}{\Delta A} \left[\left(\frac{\gamma - \frac{1}{M^2}}{\gamma - 1} \right) \frac{L}{C_{\mathbf{p}} \mathbf{T}} - 1 \right] \Delta \mathbf{g}$$
 (3.8)

If the ϵ is less than the assumed critical value then the same calculations are carried out at step $T + \Delta T$ until the critical value of ϵ is equalled or exceeded. If exceeded, a bracketing procedure is employed to improve the estimate.

All quantities computed for Δg at values of $\epsilon < \epsilon_{\text{critical}}$ are discarded, and it is assumed that there has been no condensate formed prior to $\epsilon = \epsilon_{\text{critical}}$

The choice of Δx in equation (5.8) will effect directly the magnitude of N and of Δg in equation (5.9). ΔA in equations (3.5) and (3.8) is also a function of Δx so that in the evaluation of ϵ the effect of Δx is nullified. Calculations have been



performed for values of Δx ranging from .01 to 1.0 cm to verify that the quantity has no effect on the prediction of the point of onset of condensation. Since the Δx that will be used for incrementing the calculations through the condensing portion of the nozzle will be a required input to the computer program, it is advantageous to use that same Δx in evaluating (5.8).

4. The condensing portion of the flow requires a joint solution of the nucleation and growth equations and the diabatic flow equations. The calculations are performed for increments of Δx starting from the onset of condensation. Values are estimated of p, T and U at the point i and Δg_i is calculated from the equations

$$r*_{i} = \frac{2\sigma \mu}{\rho_{I} RT \ln p/p_{\infty}}$$
(4. 5)

$$J_{i} = \left(\frac{p}{kT}\right)^{2} \frac{1}{\rho_{L}} \left(\frac{2\sigma\mu}{\pi N_{A}}\right)^{1/2} e^{-\frac{4\pi\sigma r^{2}}{3kT}}$$
(4.8)

$$N_{i} = J_{i} A_{i} \Delta x_{i}$$
 (5.8)

$$\Delta r_{j} = \frac{\alpha}{L} \frac{p}{\rho_{L}} \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{k N_{A}}{\mu T}\right)^{1/2} (T_{S} - T) \frac{\Delta x}{U}$$
 (4. 10)

$$r_{ij} = r_{i(j-1)} + \Delta r_{j}$$
 (5. 10)

$$\Delta g_{j} = \frac{4\pi \rho_{L}}{\dot{m}} \left[\sum_{i=1}^{j-1} \dot{N}_{i} r_{ij}^{2} \Delta r_{j} + \frac{1}{3} \dot{N}_{j} r_{j}^{*3} \right]$$
 (5. 11)

$$g_j = g_{j-1} + \Delta g_j$$
 (5. 12)



The subscripts i and j are numbered increments of x starting from the condensation point. i acts as a label for each group of droplets of a particular size and denotes the particular increment in which these drops originated as critical sized drops. j denotes the increments presently under consideration. Thus a designation r_{13} denotes droplets which were formed as critical drops in increment 1, have undergone the growth Δr_2 , and are now undergoing the growth Δr_3 .

Using the above approximate values of Δg and g and the unknown values of ΔA and A the equations from Section II are solved for p, T, ρ and U.

$$\frac{\Delta \rho}{\rho} + \frac{\Delta U}{U} + \frac{\Delta A}{A} = 0 \tag{2.7}$$

$$\frac{\Delta p}{p} = -\frac{U\Delta U}{(1 - g)\frac{R}{\mu}T}$$
 (2.8a)

$$\frac{\Delta p}{p} = \frac{\Delta \rho}{\rho} + \frac{\Delta T}{T} - \frac{\Delta g}{(1 - g)}$$
 (2.9)

$$U\Delta U + C_{p} \Delta T - L\Delta g = 0 \qquad (2.12)$$

The solution of the flow equations is accomplished by the following iterative procedure:

- a. assume ΔU and compute $U_j = U_{j-1} + \Delta U$
- b. solve (2.12) for ΔT and compute $T_i = T_{i-1} + \Delta T$
- c. solve (2.7) for $\Delta \rho/\rho$
- d. solve (2.9) for $\Delta p/p$
- e. solve (2.8a) for ΔU and check with value from step (a). Improve the assumed ΔU and continue until a solution is obtained.



These corrected values of p, T and U are now used to resolve the equations for Δg , and the process is continued until a set of flow parameters which satisfy both sets of equations is obtained.

This iterative procedure is continued for each increment Δx up to a specified x_{max} , usually the end of the nozzle.

This set of equations could be evaluated from the saturation point onward in order to obtain a more accurate prediction of the onset of condensation. It is obvious, however, that the magnitude of the calculations involved is formidable; and, the slight error induced by attempting to predict the point of onset of condensation, does not justify the refinement. This is especially true since the approximations in the basic equations are so gross.

C. Saturated Equilibrium Expansion

The saturated equilibrium expansion is a gradual process with condensation starting at the saturation point and equilibrium flow being maintained throughout. This occasionally occurs for slow expansions of certain vapors and for cases in which the impurity content is high. In this analysis the saturated equilibrium expansion is presented only as a comparison with the supersaturated case.

The calculations are greatly simplified in that the mass fraction of condensate can now be specified by the Clausius-Clapeyron equation

$$\frac{\mathrm{dp}}{\mathrm{dT}} = \frac{\mathrm{L}\,\mu}{\mathrm{R}} \frac{\mathrm{p}}{\mathrm{T}^2} \tag{2.3}$$



This equation and the flow equations (2.7), (2.8), (2.9) and (2.12) usually are integrated and expressions are written for each parameter (see Wegener (14) or Daum (10)). By proper manipulation and combination the integrated equations can be reduced to one involving g.

$$g = \frac{C_p}{L} T \ln \frac{T}{T_{sat}} + \left(1 - \frac{T}{T_{sat}}\right) . \qquad (5.13)$$

However, in this analysis the flow equations are programmed in the incremental form for the supersaturated case, so it is convenient to write (5.13) in the form

$$\Delta g = \frac{C_p}{L} T_i \ln \frac{T_i}{T_{sat}} + \left(1 - \frac{T_i}{T_{sat}}\right) - g_{i-1}$$
 (5.14)

and to use this for the Δg expression in a solution similar to that used for supersaturation.

- 1. The saturation point is established in the same manner as for the supersaturated case. Small increments of length, Δx , are started at the saturated point.
- 2. An incremental increase in the mass fraction of condensate, Δg , is assumed for the step Δx . With assumed value of Δg and known value of A the flow equations are solved for p, ρ , and T.

$$\frac{\Delta \rho}{\rho} + \frac{\Delta U}{U} + \frac{\Delta A}{A} = 0 \tag{2.7}$$

$$\frac{\Delta p}{p} = -\frac{U\Delta U}{(1-g)\frac{R}{\mu}T}$$
 (2.8a)



$$\frac{\Delta p}{p} = \frac{\Delta \rho}{\rho} + \frac{\Delta T}{T} - \frac{\Delta g}{(1 - g)}$$
 (2.9)

$$U\Delta U + C_{p} \Delta T - L\Delta g = 0$$
 (2. 12)

Equation (5.14) is solved to check and correct the assumed value of Δg and an iterative procedure is established to obtain a satisfactory solution of the five equations. Again this is continued in a step by step process until the solution is complete.



VI. DIGITAL COMPUTER PROGRAM

A major task in this study has been the adaptation of the mathematical analysis of Section V to the digital computer. The description contained herein is presented for the future user of the program and in no way covers the myriad of detours encountered between the input and output statements.

The Computer Center of The University of Michigan has developed a Michigan Algorithmic Decoder (MAD) computer program which compiles much faster than the commonly used FORTRAN program. The computer program for this investigation has been written in the MAD language and can be translated into FORTRAN if desired. The IBM 7090 computer program for the condensation of a pure vapor is presented in Appendix B.

The program has been subdivided into a main program and six subroutines. The subroutines enable easier modification of the program and provide a greater flexibility in its use. Statements as to the function of each of the calculations, the input parameters, and the obtainable results are provided in the program at the beginning of each subroutine. Appendix B also includes a list of the program symbolic names assigned to the parameters used in the equations of Section V.

A brief summary of the subroutines follows:

- 1. Isentropic flows (IFLOWS)—Given T, this program solves the isentropic flow equations for p, ρ , U, M, and A.
- 2. Condensation Flow (CFLOW) For given g and A, this program solves the diabatic flow equations (2.7 through 2.12) for p, T, ρ , M, and U.



- 3. Nucleation Theory I (NUCLE1) From nucleation theory equations (4. 5, 4. 8, 5. 8 and 5. 9), NUCLE1 computes the condensate formed due to the nucleation of critical sized drops only, i. e., growth is not included in this portion. This subroutine is used to determine condensate formed for that portion of the main program which determines the point of onset of condensation.
- 4. Nucleation Theory II (NUCLE2)—This subroutine evaluates the growth equation (4.10). NUCLE2 is used in conjunction with NUCLE1 to determine the amount of condensate present for all calculations downstream from the point of onset of condensation.
- 5. Nozzle (NOZZLE) The geometry of the nozzle is placed in this subroutine, from which A, ΔA , or x can be determined.
- 6. Vapor Parameters (FRHOL, FL, FSIGMA)—The parameters $\rho_{\rm L}$, L and σ are placed in this subroutine as functions of T or as constants and are evaluated as called upon by the Main Program.

The Main Program consists primarily of a proper utilization of the subroutines. The operations by the Main Program appear in the following order:

- 1. Read in the input data.
- 2. Use IFLOWS to expand isentropically from stagnation conditions.
- 3. Match isentropic equations to saturation curve to determine saturation point.
- 4. Use IFLOWS for expansion past the saturation point and calculate Δg from NUCLE1.
- 5. Evaluate epsilon equations (3. 5 or 3. 8) to determine onset of condensation.



6. Downstream of the onset of condensation, a joint solution of NUCLE1, NUCLE2, and CFLOW is obtained at each increment, Δx, and the parameters x, N, Δx, A, ΔA, P, ρ, T, U, M, r*, r, Δr, Δg and g are stored for later print out.

The saturated equilibrium expansion is compiled in a very simple program and need not be presented at this time.

The Nozzle and Vapor Parameter Subroutines are included in a Program Common such that any of the included parameters, when used in the Main Program, are automatically evaluated and returned.

Conditional statements are inserted in the program to account for the possibility of condensation occurring in either the converging or diverging portions of the nozzle, the possibility of reaching the end of the nozzle without any condensation having occurred, and the failure of the iteration of NUCLE1 and NUCLE2 with CFLOW to converge.

The development of the equations is such that any consistent set of units can be used for the problem. However, it was found that minimum scaling was necessary if the problem was worked in a cgs system of units. The problem, as written, is compatible with the cgs system of units and a list of the proper input data is presented in Appendix C.



VII. CALCULATIONS AND RESULTS

The calculations performed in this study are divided into four parts:

- 1. A test of the program by hand calculations and a test of the method by comparing the results for a nitrogen expansion with the experimental results of Willmarth (3).
- Justification of the assumptions of small radii, no drag, and accommodation coefficient approximately equal to one in the basic assumptions. Verification of the prediction procedure for the onset of condensation.
- 3. A variation of latent heat, specific heat, surface tension, and nozzle geometry for the nitrogen expansion to observe the induced effect of each parameter.
- 4. Application of the theory to metal vapors by computing the expansion from an initial pressure of approximately one atmosphere of copper, tin, lead, and zinc vapors.

A. Validation of the Program

The input data for the calculations performed in this study are tabulated in Table C-1 of Appendix C. A reference to Nitrogen (I), Zinc (I), etc., indicates the set of input data from which the indicated results were obtained. Any additional modifications of the input data, such as a change in σ , L, or nozzle geometry, are listed directly on the plot of results. An explanation of the input data required, the proper units for each parameter, and the references (20-24) from which the vapor properties were obtained is also presented in Appendix C.



Initially the computer program was divided into small segments and hand calculations were performed for Nitrogen (I) to verify the computer results. With the assurance that each small segment was working properly, the entire program was assembled and hand calculations were performed to spot check the calculations of the saturation point, the point of onset of condensation, and the first few incremental steps of the condensing flow regime.

With this degree of confidence in the program, the next step was to check the theoretical results with known experimental results. The Nitrogen (I) input data is designed to approximate an experimental test of the condensation of nitrogen performed by Willmarth (3).

Nitrogen properties from NBS Circular 564 (24) and the International Critical Tables (23) required extrapolation below 70° K for the surface tension and the latent heat of vaporization. These values are generally valid only to within $\pm 10\%$ and, as will be shown later, this becomes extremely critical in the case of the surface tension. The vapor pressure curve for nitrogen is reasonably well known, and it was approximated by the Clausius-Clapeyron equation (see Fig. C-1).

For comparison with experiment the calculations for nitrogen were carried out in full from the saturation point onward and no attempt was made to predict the point of onset of condensation. A comparison of the experimental results of Willmarth (3) to the theoretical prediction of the condensation of Nitrogen (I) is presented in Figure 1. The theoretical curve for Nitrogen (I) shows a degree of supersaturation of approximately 3. 5 degrees (20%) lower than is indicated by experimental results. This is expected in that the amount of impurities in the experimental nitrogen was unknown and this advanced nucleation would cause an early break. However, of greater importance is the degree of



uncertainty in the extrapolation of the available surface tension data. In anticipation of the effect of σ on the theoretical results, a second extrapolation was chosen for σ . The σ equation for Nitrogen (II) remains within the \pm 10% accuracy of the original surface tension data and, in actuality, gives a value for σ which is only 7% less than the σ from Nitrogen (I) at the onset of condensation.

The theoretical prediction for the condensation of Nitrogen (II) compares most favorably with the experimental results in Figure 1. The strong influence shown by only a 7% change in σ will be discussed more fully at a later point in the discussion. Figure 2 presents a more complete comparison of the theoretical results for Nitrogen (II) as compared to the experimental results of Willmarth (3). The isentropic and saturated equilibrium expansions are also presented in this figure. The theoretically calculated results presented in Figure 2 employ the full calculation of the nucleation and flow equations for the entire length of the nozzle. This is significant in that the flow properties prior to the "condensation shock" lie on the isentrope and the flow properties after the "shock" tend to approach the saturated equilibrium expansion. This is the expected result, and it gives further confidence in the program.

The experimental points of Willmarth (3) fall on the isentrope as well as along the "condensation shock", which indicates a proper estimate of the physical expansion and validates the program. The close correlation between theoretical and experimental results within the "shock" itself lends further support to the basic nucleation theory of the condensation process.



Willmarth (3) obtained the pressure results, p, p_0 and p_0' by direct measurement. The effective area ratio, $(A/A^*)_{eff}$, temperature, T, and mass fraction of condensate, g, were then calculated from the measured quantities by a joint solution of the flow equations.

B. Justification of Assumptions

1. Drop Size

A typical distribution of maximum and minimum droplet radius is presented in Figure 3 for the Nitrogen (I) expansion. Note the very short span over which the nucleation of critical sized drops, J curve, takes place. The average critical sized drop has a radius of 4.5×10^{-8} cm, and the largest particles which leave the nozzle have a radius of 8×10^{-7} cm. The radius of the nitrogen molecule from Loeb (25) is approximately 1.5×10^{-8} cm and calculated mean free paths vary from the order of 10^{-4} cm at the onset of condensation to 10^{-3} cm near the nozzle exit. According to Stever (5) the drop radius is larger than the minimum required to contain the 10-12 molecules necessary for the application of macroscopic theory.

Therefore it is not unreasonable to assume that small drops are the general rule, that the no drag approximation is valid, and that since r << mean free path the samll drop growth equation can be used.

2. Accommodation Coefficient

The effect of a variation in α is presented in Figure 4. Small variations near the value of $\alpha=1.0$ have very little effect. However, since the growth equation is a direct function of α , the curve for $\alpha=0.1$ differs markedly from $\alpha=1.0$. Fortunately, the known values for α are from 0.8 to 1.0 so that the choice of $\alpha=1.0$ is a



reasonable one. The computer program is so constructed that accurate values of α , when known, can be inserted as input data.

An additional feature of Figure 4 is the indication that growth has little effect up to the "break" point but thereafter controls the remainder of the condensation process. This is further brought out by the plot of J in Figure 3, which indicates the rapid nucleation of a large number of particles to start the "shock" and then a continuing growth of these particles until saturated equilibrium conditions are met.

3. Point of Onset of Condensation

From the previous discussion and from Figure 3, it appears that little or nothing happens in regard to condensation until a degree of supersaturation is reached for which the critical drop radius is very small. As r^* from equation (4.5) becomes small the exponential term, which contains r^{*2} , ceases to be the predominant term in equation (4.8) and J increases rapidly.

$$r^* = \frac{2\mu\sigma}{\rho_L RT \ln p/p_{\infty}}$$
 (4. 5)

$$J = \left(\frac{p}{kT}\right)^{2} \frac{1}{\rho_{L}} \sqrt{\frac{2\sigma\mu}{\pi N_{A}}} e^{-\frac{4\pi \sigma r^{*2}}{3kT}}$$
(4.8)

The epsilon of Section III should then predict the approximate point of onset of condensation. Several calculations for various values of ϵ are presented in Figure 5. ϵ = 0 indicates that the full calculation of the nucleation and flow equations was carried out from the saturation point onward. The choice of epsilon results



in only a minor error when compared to the possible 10% error in surface tension. Epsilon values of 10^{-3} and 10^{-4} give almost identical results, thus ϵ = .001 appears to be a suitable choice for the expansion of nitrogen.

Also in agreement are Head's (2) calculations for water vapor in which he indicates that the attainment of $J = 10^{16}$ droplets per centimeter cubed per second signifies the point at which the condensation shock will break away from the isentrope. Several calculations on the computer indicate that $J \doteq 10^{16}$ at the break-away point for nitrogen also. At present, however, this author sees no justification for predicting that this will be true for other vapors as well.

C. Variation of Parameters

1. Surface Tension

As indicated previously, the variation of σ is the most critical aspect of the theoretical prediction of the condensation phenomenon. From equations (4.5) and (4.8) it can be seen that σ enters the exponential term of J as a third power. Thus for a 10% change in σ the nucleation rate changes by several orders of magnitude. Figure 6 and Figure 7 present several variations in σ to show the large effect that this parameter has on the degree of supersaturation. Later results will show that the effect of other parameters is minor when compred to surface tension.

There appears here a possible method of improving the surface tension data. The results of a closely controlled experimental vapor expansion could be used as a reference plot and surface tension varied on the computer until a matching plot is obtained. Providing



the other parameters are reasonably well known, this should provide a better estimate of σ than merely extrapolating a curve far away from the few experimentally determined values that are available.

2. Specific Heat

 C_p is reasonably well known and only varies a few percent over the range considered in this analysis. For this analysis C_p is chosen as a constant, and from the plot in Figure 8 the constant assumption for C_p appears reasonable. The effect of a 10% variation in C_p is negligible when compared to an equivalent uncertainty in σ .

3. Latent Heat of Vaporization

Latent heat is generally a weak function of temperature. For Nitrogen (I) the variation in L is only 9% over the range of temperature from saturation to the nozzle exit. From the plot of variations in L presented in Figure 9 it is evident that the constant latent heat assumption in the basic equations is a reasonable assumption and any variation in L is negligible when compared to the effect of an equivalent variation in σ .

4. Nozzle Geometry

The condensation process is a function of time, so it is expected that the rate of expansion should have some effect on the "condensation shock." Theoretical calculations were performed for the Nitrogen (I) expansion in a two dimensional nozzle for which the exit half-angle was varied from 9.75 to 45 degrees. Nozzle lengths were selected so that a Mach 8 nozzle was used for each run. The results of varying the rate of expansion for Nitrogen (I) are presented in Figure 10 and Figure 11. In Figure 10 it is noted



that the faster expansion causes the vapor to supersaturate to a lower temperature before the onset of condensation. The "condensation shock" is thinner for the fast expansion, it is (in physical dimensions) 3 cm for the $\theta_{1/2} = 45^{\circ}$ expansion versus 5 cm for the $\theta_{1/2} = 9.75^{\circ}$ expansion. $\theta_{1/2}$ is the nozzle exit half-angle.

This is somewhat misleading because, for Figure 11, in which all nozzles are referenced to a non-dimensional length for a Mach 8 nozzle, the faster expansion tends to smear out over a broader relative length. The plot of the percent of condensed vapor in Figure 11 indicates that the higher the rate of expansion the less moisture is formed in the nozzle. It appears that for sufficiently high rates of expansion a condensation free flow can be obtained. This has been borne out by "condensation free" experiments in the past.

D. Application to Metal Vapors

As stated in Section V, the theory as developed herein should apply to metal vapors. The primary interest here is in the finding of a metal vapor that will condense in a highly expanded flow and that is suitable for laboratory experimental use. Hill (11) has predicted that sodium and potassium will condense; however, these vapors introduce critical handling problems. Copper, zinc, tin and lead appear to have possible experimental use, with copper being the preferred vapor of the four.

Theoretical calculations were performed for a two-dimensional nozzle with a constant slope diffuser for the metal vapor input data listed in Appendix C.



1. Copper

Fortunately, copper vapor is theoretically predicted to condense for a fairly rapid expansion in a two-dimensional nozzle with a 20 degree diffuser half-angle. The results are presented in Figure 12 for an expansion in a Mach 10 nozzle from an initial pressure of approximately one atmosphere and an initial temperature of 3000°K. The "condensation shock" occurs very near the throat, and the change is very rapid with the "shock" spanning less than a centimeter of nozzle length. The average critical drop radius is approximately 3 x 10⁻⁸ cm and the maximum droplet formation rate is of the order of 10¹⁹ drops per centimeter cubed per second. Again the onset of the condensation appears to be marked by a value of $J = 10^{16}$ or 10¹⁷ drops per centimeter cubed per second. Copper could be a suitable choice for experimental work in rapid expansions because the large fraction of condensate formed in this theoretical solution indicates that higher rates of expansion and higher initial temperatures and pressures probably could be used without resulting in a "condensation free" expansion.

2. Zinc

Two computer runs were made for zinc, and neither run predicted any detectable amount of condensate. Zinc (I) was computed for a 45 degree diffuser half-angle and initial pressure and temperature of approximately one atmosphere and 1500° K respectively. The results of this calculation are presented in Figure 13 where a sufficient number of the calculated points are plotted along the isentrope to show that the expansion is essentially isentropic. This indicates a negligible amount of condensation. The tabulated calculations from the computer give a maximum g of 1.48 x 10^{-8} at the nozzle exit.



The maximum nucleation rate obtained is $J = 2 \times 10^{12}$ drops per centimeter cubed per second and the critical drop radius is 2×10^{-8} cm. It was anticipated that a slower expansion with a lower starting temperature would predict a detectable amount of condensate. Zinc (II) was run on the computer for a 20 degree diffuser and a pressure and temperature of one atmosphere and 1300°K respectively. The results in Figure 13 again plot along the isentrope and indicate no condensate. The maximum g of 4.8 \times 10⁻⁵ for the Zinc (II) run indicates some movement toward condensation. The maximum nucleation rate of $J = 3 \times 10^{14}$ drops per cubic centimeter per second is obtained at a vapor temperature of 375°K and the critical drop radius is again 2 x 10⁻⁸ cm. $J = 10^{14}$ value with no condensate formed lends support to the $J = 10^{16}$ criterion for the onset of condensation. A slower expansion of zinc probably would produce a condensation shock; however, this would be out of the desired rapid expansion regime. From the results of the Zinc (I) and Zinc (II) runs it appears that for rapidly expanding flows zinc vapor may not condense.

3. Tin and Lead

Unfortunately, the computer runs for tin and lead failed to converge in the CFLOWS Subroutine. The reason for this is not immediately apparent, and a further investigation will have to be made before any definite conclusions can be drawn. However, the few points that were calculated show promise that both tin and lead will condense in a rapid expansion.



VIII. CONCLUSIONS

An adaptation of the digital computer to the analysis of the condensation of a flowing vapor is possible, and the program for a pure vapor is presented herein. Theoretical predictions of the condensation of nitrogen, copper and zinc indicate the following:

- 1. The nucleation theory of Frenkel (13) provides a reasonable approximation to the rate of formation of condensate in a flowing vapor.
- 2. The theoretical prediction for the condensation of nitrogen compares surprisingly well with the experimental results of Willmarth (3).
- 3. A small drop size is the general rule. The critical drop radius is of the order of 10^{-8} cm and droplets of maximum growth rarely exceed 10^{-6} cm.
- 4. The nucleation rate controls the onset of condensation, and a prediction procedure based on this parameter might prove more useful than the one proposed herein.
- 5. The growth equation plays a predominant role once condensation has started and a more accurate expression would be beneficial.
- 6. The surface tension is the most influential parameter. Generally the value of σ is uncertain and this leads to the largest source of error in the program.
- 7. Values of specific heat and latent heat of vaporization are not critical, and treating these parameters as constants is a reasonable assumption.
- 8. The condensation process is very sensitive to rates of expansion, and for rapidly expanding vapors a "condensation free" expansion is possible.



- 9. Copper vapor will condense in rapidly expanding flows and appears suitable for experimental work in the condensation of metal vapors.
- 10. Zinc vapor does not condense for high rates of expansion from one atmosphere pressure, and runs for lower pressures and temperatures are recommended.



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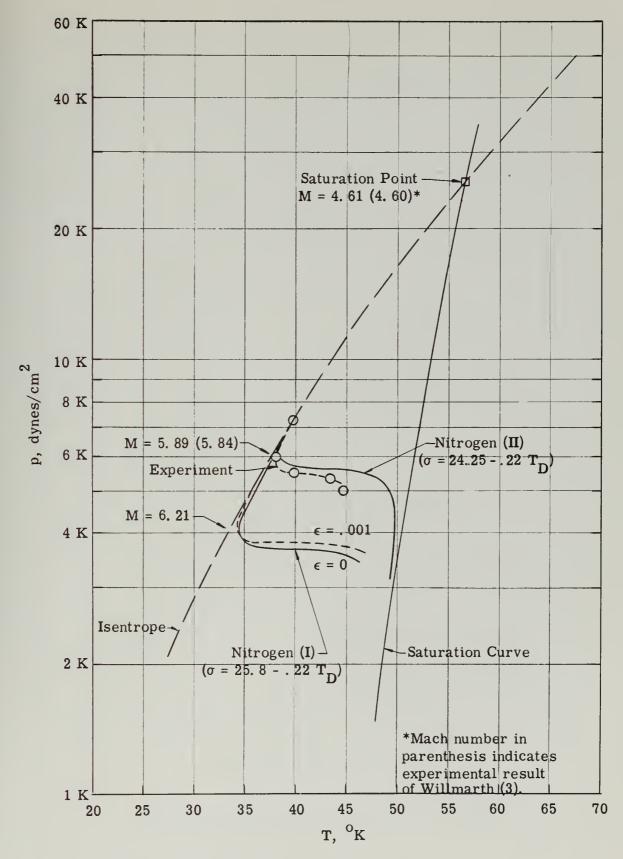


Figure 1. Theoretical Results for Nitrogen Compared to Experimental Results of Willmarth (3).



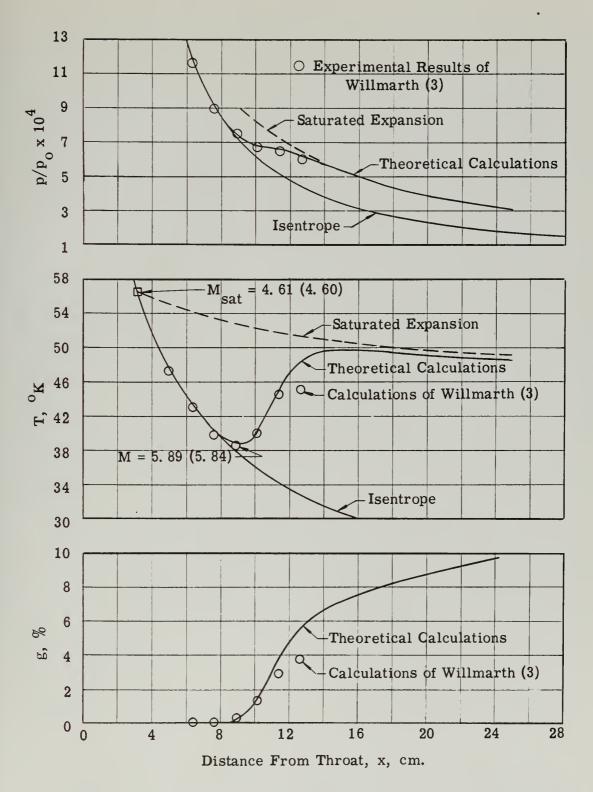


Figure 2. Theoretical Prediction of the Condensation of Nitrogen (Π) Compared to Experimental Results.



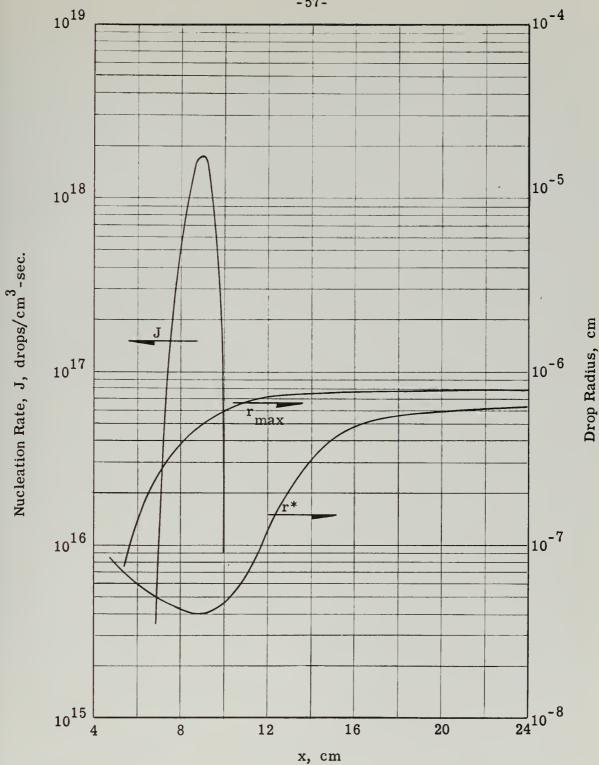


Figure 3. Typical Expansion of Nitrogen (I) Presenting Variation of Nucleation Rate, Maximum Droplet Radius and Critical Droplet Radius Along Nozzle Axis.



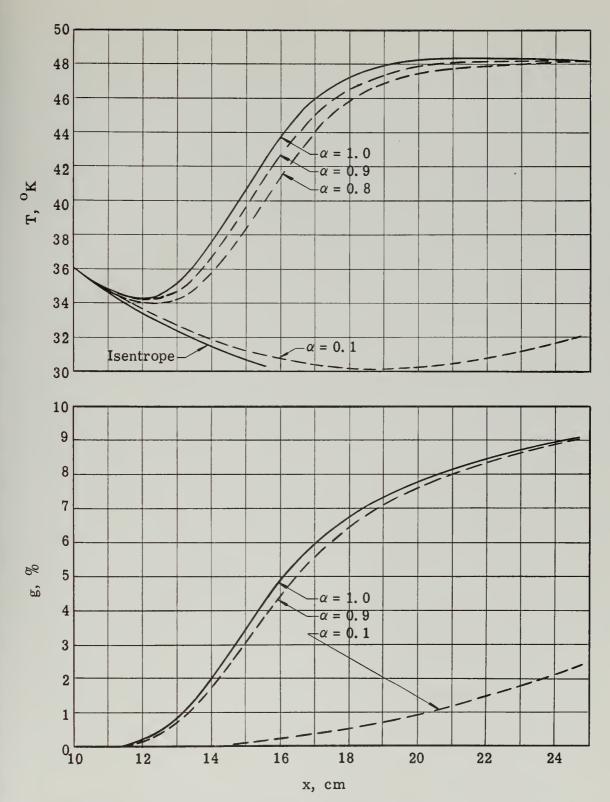


Figure 4. Theoretical Prediction of the Effect of a Variation in the Accommodation Coefficient on the Condensation of Nitrogen (I).



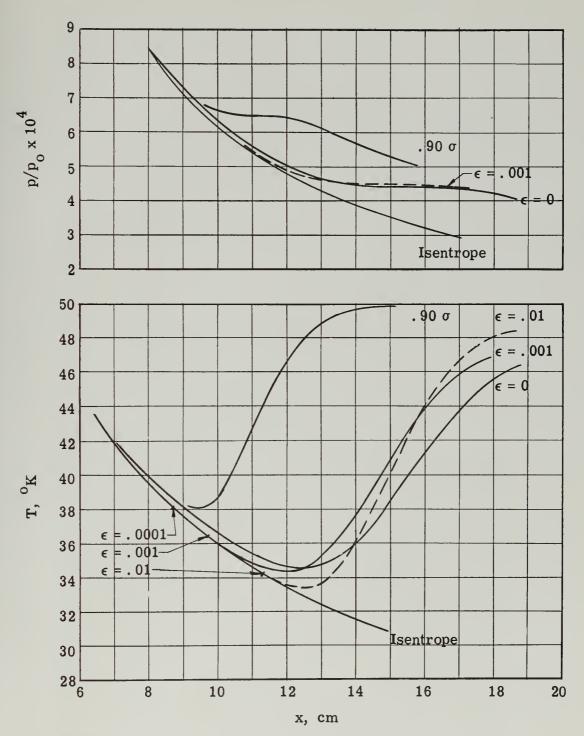


Figure 5. Effect of Choice of ϵ as a Predictor of the Onset of Condensation for Nitrogen (I).



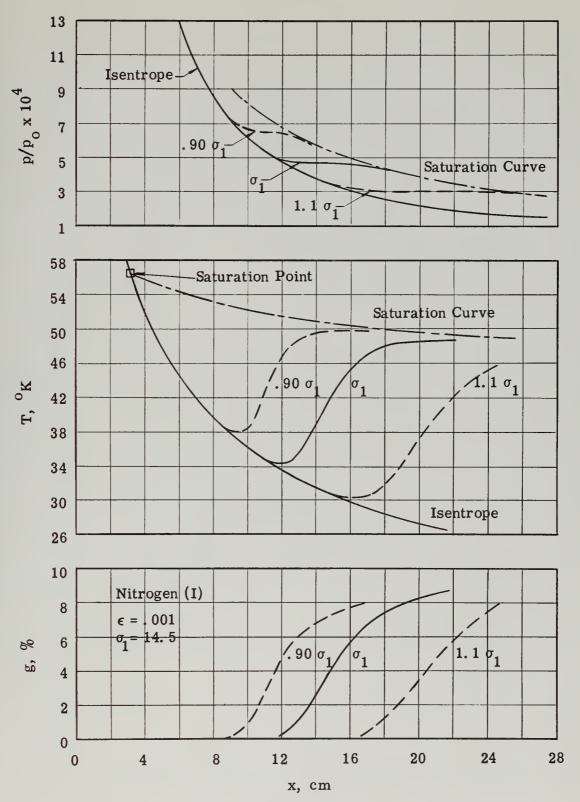


Figure 6. Effect of ± 10% Variation in Surface Tension on the Theroetical Prediction of the Condensation of Nitrogen.



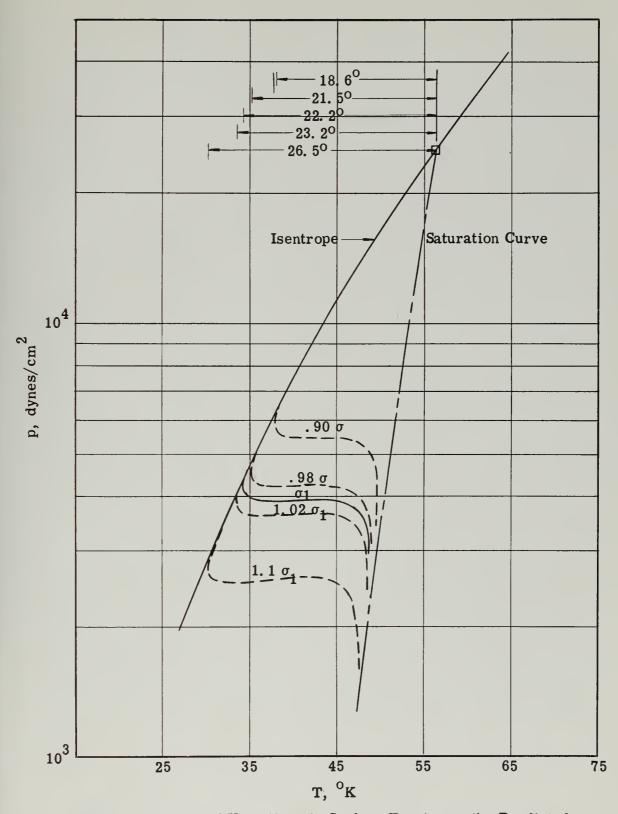


Figure 7. Effect of Variations in Surface Tension on the Predicted Supersaturation of Nitrogen.



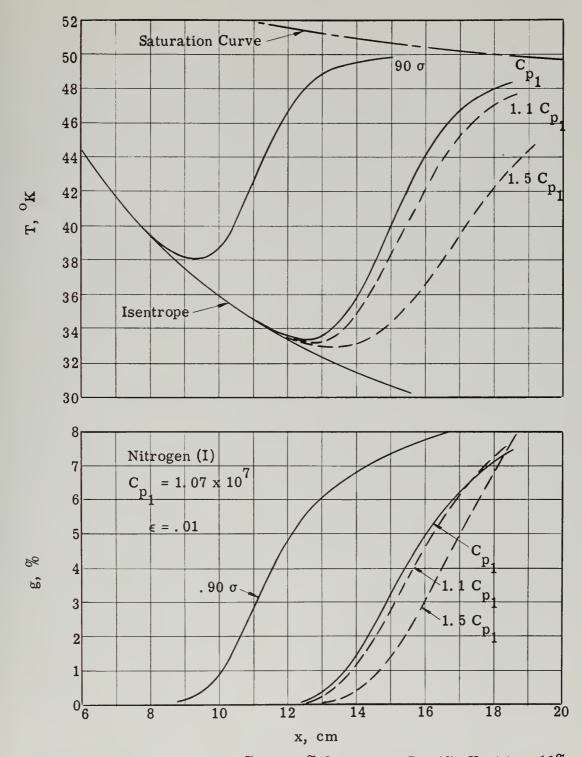


Figure 8. Comparison of 10% and 50% Changes in Specific Heat to a 10% Change in Surface Tension for Nitrogen (I).



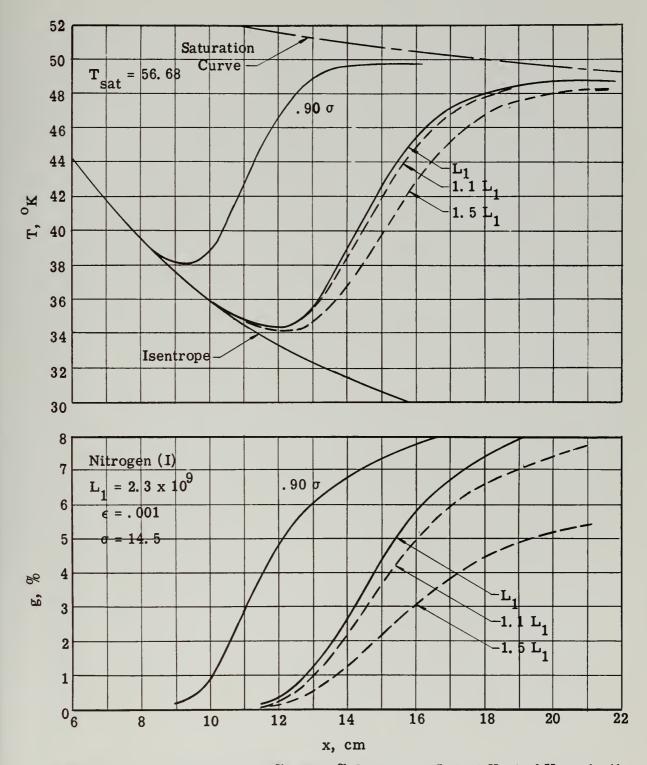


Figure 9. Comparison of 10% and 50% Changes in Latent Heat of Vaporization to a 10% Change in Surface Tension for Nitrogen.



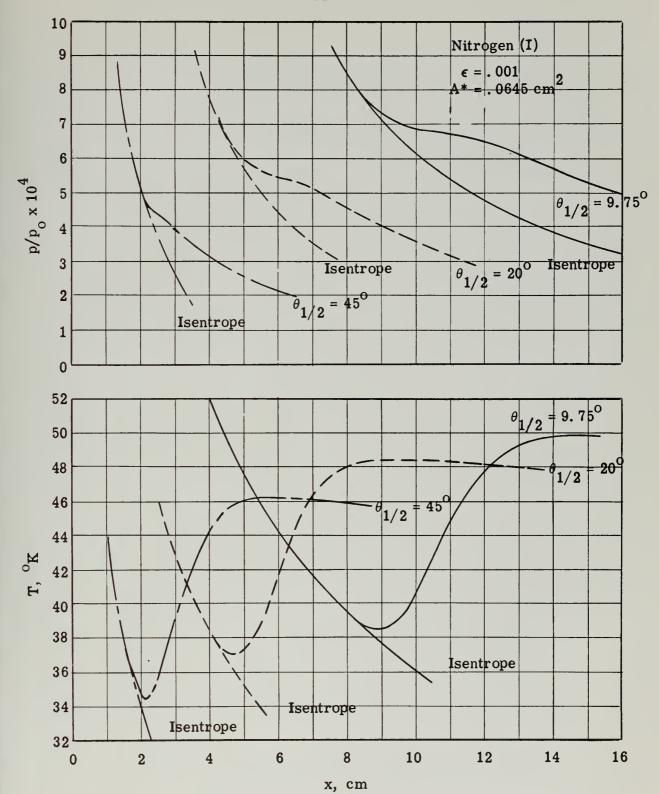


Figure 10. Theoretical Expansion of Nitrogen (I) for a Two-Dimensional Nozzle with Varying Exit Half-Angle, $\theta_{1/2}$.



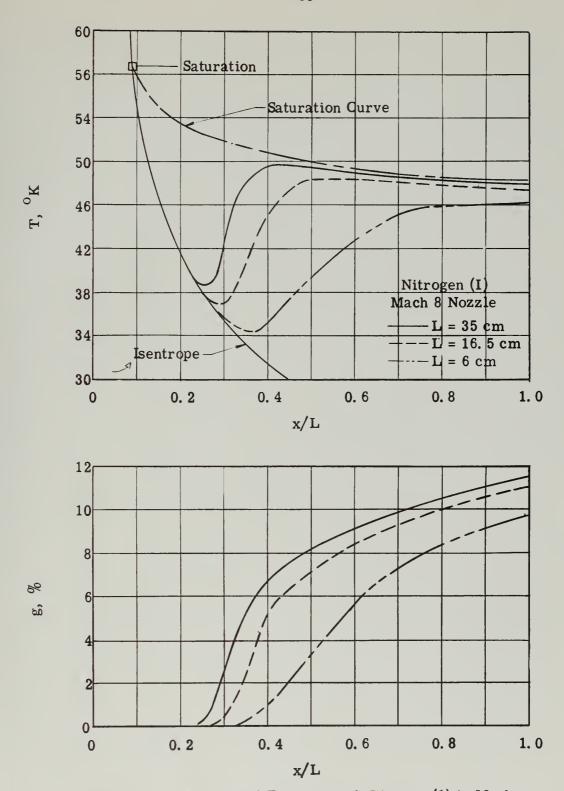


Figure 11. Theoretical Expansion of Nitrogen (1) in Mach = 8 Nozzle of Lengths 35, 16.5, and 6 cm.



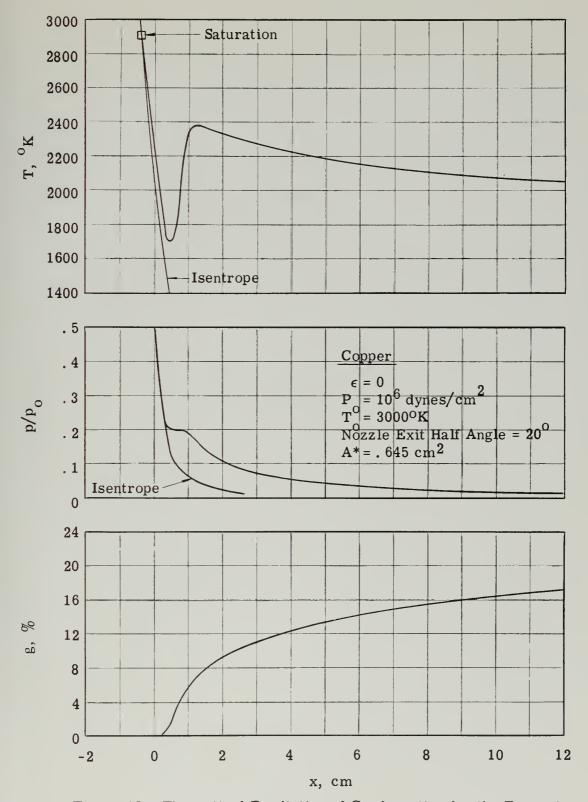


Figure 12. Theoretical Prediction of Condensation for the Expansion of Copper Vapor in a Two-Dimensional Nozzle.



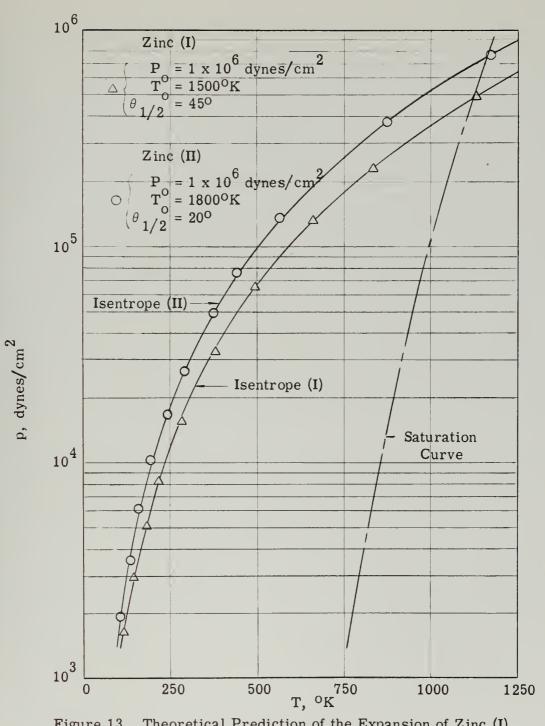


Figure 13. Theoretical Prediction of the Expansion of Zinc (I) and Zinc (II) Vapor Indicating No Condensation.



Appendix A

DERIVATION OF THE NUCLEATION RATE EQUATION

This is in no way intended to be a complete derivation of the nucleation rate equation. The full derivation can be found in complete detail on pages 366 through 400 of Frenkel (13). A scant derivation is presented in Stever (12), pages 532 to 540.

There appears to be an error of π in the final equation presented by Frenkel, so enough of the derivation will be reproduced here to clear up this discrepancy. The solution is a statistical problem of kinetic theory.

In an equilibrium distribution of droplets where $\phi_{\rm v} < \phi_{\rm liq}$ the following relation must hold.

$$N_n S_n \alpha_n = N_{n-1} S_{n-1} \beta_{n-1}$$
 (A.1)

where ϕ_v and ϕ_{liq} are the thermodynamic potentials of the vapor and liquid drops, respectively. N_n and N_{n-1} are the number of droplets containing n and (n - 1) molecules, respectively. S_n and S_{n-1} are the surface areas of droplets containing n and (n - 1) molecules, respectively. α_n is the probability that one molecule leaves a unit surface area of a droplet containing n molecules.

 eta_{n-1} is the probability that one molecule condenses on a unit surface area. Assume $lpha_n$ and eta_{n-1} to remain valid for the non-equilibrium case $(\phi_{liq} < \phi_v)$ and modify the distribution N_n to a non-equilibrium distribution f_n . The equation will no longer balance so (A. 1) become s



$$J_{n} = f_{n-1} S_{n-1} \beta_{n-1} - f_{n} S_{n} \alpha_{n} \neq 0$$
 (A. 2)

where J_n represents the increase per unit time of the class (n) due to condensation of the vapor on the surface of droplets in class (n - 1) over the number, which, owing to evaporation, pass from the class (n) to the class (n - 1).

The rate of change of the number of drops of a given class is determined from (A. 1) and (A. 2) to be

$$\frac{\partial f}{\partial t} = J_n - J_{n-1} \tag{A.3}$$

Frenkel employs the method of Zeldovich which utilizes the feature of the sharp maximum of $\Delta\Phi$ at n* to solve the equation. By considering only values of n > 10 say, quantities appearing in the equation will only vary slightly when n is changed by 1 and can be treated as functions of a continuous variable. Equation (A. 3) can then be integrated and the result is presented as equation (27b) on page 396 of Frenkel (13).

$$J = N_n D(n^*) \left(\exp - \frac{\Delta \Phi (n^*)}{kT} \right) \sqrt{\frac{\gamma}{2\pi kT}}$$
 (A. 4)

where N_n = $\frac{p}{kT}$ = number of molecules in the supersaturated vapor D(n*) = S(n*) β = diffusion coefficient = $(4\pi)^{1/3} 3^{2/3} V_{liq}^{2/3} n^{2/3} \beta$ $\beta = \frac{p}{\sqrt{2\pi \, mkT}}$ $\Delta \Phi = \frac{4}{3} \pi \, \sigma \, r^{2/3} + \frac{2}{3} (\phi_{liq} - \phi_{v})/n^{2/3}$

substituting these values into (A. 4) produces the equation

$$J = 2r^{2} \left(\frac{p}{kT}\right) \left(\exp -\frac{4\pi\sigma r^{2}}{3kT}\right) \sqrt{\frac{1}{3} \frac{(\phi_{\text{liq}} - \phi_{\text{v}})}{mn^{2}}}$$
(A. 5)



or, writing in the form of Frenkel's final equation (28a)

$$\frac{n*J}{N_{n}} = 2r^{2} \frac{p}{kT} \left(\exp -\frac{4\pi \sigma r^{2}}{3kT} \right) \sqrt{\frac{1}{3} \frac{(\phi_{liq} - \phi_{v})}{m} n^{2}}$$
 (A. 6)

In comparing (A. 6) with Frenkel's equation (28a), it is noted that Frenkel does have an extra factor of π in the coefficient as noted by Courtney (9) and others.

The desired equation for this analysis is obtained by substituting the value of $(\phi_{liq} - \phi_{v})$ from the critical radius equation $r^* = \frac{2\sigma V_{liq}}{\phi_{liq} - \phi_{v}}$ and the value $n^* = \frac{1}{V_{liq}} \frac{4}{3} \pi r^*$ into equation (A. 5)

$$J = 2r^{*2} \left(\frac{p}{kT}\right)^{2} \left(\exp - \frac{4\pi \sigma r^{*2}}{3kT}\right) \sqrt{\frac{1}{3}} \frac{2\sigma V_{liq}}{mr^{*}} \frac{V_{liq}^{3}}{4\pi r^{*3}}$$

$$= \frac{2r^{*2}}{2r^{*2}} V_{liq} \left(\frac{p}{kT}\right)^{2} \left(\exp - \frac{4\pi \sigma r^{*2}}{3kT}\right) \sqrt{\frac{2\sigma}{\pi m}}$$

$$J = \left(\frac{p}{kT}\right)^{2} V_{liq} \sqrt{\frac{2\sigma}{\pi m}} \exp - \frac{4\pi \sigma r^{*2}}{3kT}$$
(A. 7)

To eliminate the necessity of calculating molecular values of $V_{liq} = \frac{\mu}{N_A \rho_L} \text{ and } m = \frac{\mu}{N_A} \text{, the equation for computing J in this analysis is written}$

$$J = \left(\frac{p}{kT}\right)^2 \frac{1}{\rho_L} \left(\frac{2\mu\sigma}{\pi N_A}\right)^{1/2} \exp -\frac{4\pi\sigma (r^*)^2}{3kT}$$
 (A. 8)



Appendix B

IBM 7090 DIGITAL COMPUTER PROGRAM FOR CONDENSATION IN HIGHLY EXPANDED FLOWS

Written in Michigan Algorithmic Decoder (MAD) Language

This program is valid for a pure vapor with constant specific heat and constant latent heat of vaporization.

The cgs system of units is utilized throughout and cgs values for the universal gas constant, Boltzmann's gas constant, and Avogadro's number have been included within the program.

The symbolic names of parameters used in the program are listed and defined at the beginning of each applicable section of the program.

The units for and input data required for utilization of this program are presented in Appendix C.



```
$COMPILE MAD, PRINT OBJECT, PUNCH OBJECT
                                                                MAIN OOLMAIN OOO
          R AERONAUTICAL ENGINEERING
                     NOZZLE CONDENSATION RESEARCH
          R
          R
                              MAIN PROGRAM
          R
          RRESEARCH-- J. GRIFFIN PROGRAMMING-- L. HARDING JULY 1963
          PROGRAM COMMON GAMMA, MU, B, C, CP, L, RHOL, SIGMA
START
          READ DATA
          R
         RTHIS DATA SHOULD INCLUDE
          R PZERO = INITIAL PRESSURE
          R RHZERO = INITIAL DENSITY
          R TZERO = INITIAL TEMPERATURE
          R PE = ISENTROPIC EXIT PRESSURE. THIS IS USED AS AN
                     INITIAL APPROXIMATION TO THE SATURATION PRESSURE.
          R
          R GAMMA = RATIO OF THE SPECIFIC HEATS
                = MOLECULAR WEIGHT OF THE VAPOR
= SPECIFIC HEAT AT CONSTANT PRESSURE
          R MU
         R CP
R L
                  = LATENT HEAT (NOTE VAPOR PARAMETERS SUBROUTINE)
         R SIGMA = SURFACE TENSION (NOTE VAPOR PARAMETERS SUBROUTINE)
        R C = SATURATION CURVE CONSTANT
          R B = SATURATION CURVE CONSTANT
         R ALPHA = ACCOMODATION COEFFICIENT
         R DELX = INCREMENTAL STEP IN X. THE NOZZLE CONDITIONS WILL
                    BE COMPUTED AT XCON+DELX, XCON+2*DELX, ... WHERE
                     XCON IS THE CONDENSATION POINT.
          R XRANGE = LENGTH OF INTERVAL, STARTING AT THE CONDENSATION
                     POINT, IN WHICH THE FLOW CONDITIONS WILL BE
          R
                     COMPUTED.
          R XPOINT = THE CONDENSATION POINT IS ASSIGNED A SUBSCRIPT OF
                    ZERO, ONLY THOSE POINTS WITH SUBSCRIPTS XPOINT,
         R
                     2*XPOINT, . . . WILL BE PRINTED.
          R TRANGE = PROGRAM WILL LOOK FOR A CONDENSATION POINT IN THE
                     INTERVAL (TSAT, TSAT-TRANGE), WHERE TSAT IS THE
         R
                     COMPUTED SATURATION TEMPERATURE.
          R DELTAT = INITIAL STEP SIZE USED IN LOOKING FOR CONDENSATION
                    POINT IN THE INTERVAL (TSAT, TSAT-TRANGE) .
          R PERCNT = IF EPSLON(T) EXCEEDS PERCNT IT IS ASSUMED THAT
                   CONDENSATION HAS STARTED.
         R
           PRINT COMMENT $1
                                                                     NOZ
          1ZLE CONDENSATION RESEARCH
                                      $
            PRINT COMMENT $0 INITIAL CONDITIONS$
            PRINT RESULTS PZERO, RHZERO, TZERO, PE
           PRINT COMMENT $0 CONSTANTS DEPENDING ON THE VAPORS
            PRINT RESULTS MU, CP, GAMMA, SIGMA, L
           PRINT COMMENT $0 SATURATION CURVE CONSTANTS$
PRINT RESULTS C.B
PRINT COMMENT $0 PROGRAM PARAMETERS$
            PRINT RESULTS DELX, XRANGE, XPOINT, ALPHA
           EXECUTE NOZZLE . (STHROATS, O., ASTAR)
```



52

53

56

```
FIND SATURATION POINT BY MATCHING ISENTROPIC PRESSURE
R
      SOLUTION TO THE SATURATION CURVE PRESSURE.
K
p=p=
 Z=GAMMA/(GAMMA+1.)
 T=C/(B+ELOG.(P))
 PSAT=PZERO*( (T/TZERO) .P. Z )
 TEST = . ABS . (1 . - PSAT/P) - . 001
 WHENEVER TEST. L. C. , IRANSFER 10 52
 P=P+.5*(PSAT+P)
 TRANSFER TO S1
 TSAT=T
 EXECUTE IFLOWS . (ASTAR , CP , GAMMA , PZERO , RHZERO , TZERO)
 EXECUTE IFLOW. (ASAT, MSAT, PSAT, RHOSAT, TSAT, USAT)
 Z=MSAT
 EXECUTE NOZZLE . ($INVERS$ , Z , ASAT)
 WHENEVER Z(1).E.1., TRANSFER TO S3
 PRINT COMMENT $4 THE SATURATION POINT FOUND IS NOT INSIDE
1 THE NOZZLE, THE PROGRAM WILL CONTINUE.$
 XSAT=Z
 MDOT=ASAT*RHOSAT*USAT
                              COMPUTED SATURATION CONDITIONSS
  PRINT COMMENT $2
  PRINT RESULTS PSAT, RHOSAT, TSAT
  PRINT RESULTS MSAT, USAT
  PRINT RESULTS XSAT, ASAT
  PRINT RESULTS MDCT
R
      FIND CONDENSATION POINT BY MATCHING ISENTROPIC FLOW
R
       SOLUTION TO THE NUCLEATION THEORY SOLUTION GIVING THE
R
       AMOUNT OF CONDENSATE AS A FUNCTION OF AN ASSUMED FLOW.
R
R
 DELT = DELTAT
 ITERF=0.
 TMIN=TSAT-TRANGE
 WHENEVER TMIN.L.O., TMIN=0.
                             PARAMETERS DETERMINING CONDENSATIO
  PRINT COMMENT $2
IN POINT SEARCH$
                                                    side of a property of rate E.S.
  PRINT RESULTS TSAT, TMIN, DELT
  PRINT RESULTS PERCNT
R
R
 T=TSAT
  ITER=0.
 T=T-DELT
          WHENEVER T .L. TMIN
 Z=1.
 ITERF=ITERF+1.
 DELT= .5*DELT
 WHENEVER ITERF . L . 10 . , TRANSFER TO S4
  WHENEVER Z. 5.0. TRANSFER TO ST
 PRINT COMMENT $0 TEN PASSES OVER TEMPERATURE RANGE SPECIFIED,
 1 NO CONDENSATION POINT INDICATED. $
 TRANSFER TO START
          END OF CONDITIONAL
  EXECUTE IFLOW. (A,M,P,RHO,T,U)
  7 = M
  EXECUTE NOZZLE . (SINVERSD , Z , A)
          WHENEVER Z(1) .E. O.
```



```
57
```

```
Z=0.
 TRANSFER TO S6
PRINT COMMENT $0 TEN PASSES OVER THE FULL RANGE OF THE NOZZLE
1, NO CONDENSATION POINT INDICATED.$
 TRANSFER TO START
       END OF CONDITIONAL
 EXECUTE NOZZLE . ($AREA$, X-DELX, Z)
DELA = A-Z
R
 L=FL (T)
 TDROP=C/(B-ELOG.(P))
 RHOL=FRHOL (TDROP)
 SIGMA=FSIGMA · (TDROP)
 EXECUTE NUCLEI. (A, DELX, MDOT, P, T, RAD, NDOT, DELG)
R
     COMPUTATION OF EPSILON (T)
 EPSLON=(GAMMA-(1./(M*M)))/(GAMMA-1.)
 WHENEVER M.L.1., EPSLON=1.
 EPSLON=A*(1.-(L/(CP*T))*EPSLON)
 EPSLON=EPSLON*(DELG/DELA)
 EPSLON = . ABS . EPSLON
 WHENEVER EPSLON. L. PERCNT, TRANSFER TO S5
 T=T+DELT
 DELT = .5 * DELT
 ITER=ITER+1.
WHENEVER ITER. L. LITER, TRANSFER TO S5
R
R
      LITER HALF-INTERVAL STEPS HAVE BEEN PERFORMED AND
      A CONDENSATION TEMPERATURE HAS BEEN FOUND.
R
 PRINT COMMENT $0 HAVE FOUND TEMPERATURE THAT SATISFIES THE CO
INDITIONS FOR THE CONDENSATION POINTS
 PRINT RESULTS T, DELT
 TCON=T
 EXECUTE IFLOW. (ACON, MCON, PCON, RHOCON, TCON, UCON)
 Z=MCON
 EXECUTE NOZZLE . ($INVERS$ , Z , ACON)
 WHENEVER Z(1) . E . 1 . , TRANSFER TO S8
 PRINT COMMENT $4 THE CONDENSATION POINT FOUND IS NOT INSI
1DE THE NOZZLE, THE PROGRAM WILL CONTINUE. $
 XCON=Z
 L=FL.(T)
 TDROP=C/(B-ELOG • (PCON))
 RHOL = FRHOL . (TDROP)
 SIGMA=FSIGMA · (TDROP)
 EXECUTE NUCLEI. (ACON, DELX, MDOT, PCON, TCON, RAD, NDOT, DELG)
 G=DELG
 PRINT COMMENT $4 COMPUTED CONDENSATION CONDITIONS$
  PRINT RESULTS PCON, RHOCON, TCON
  PRINT RESULTS MCON, UCON
  PRINT RESULTS XCON, ACON
PRINT RESULTS SIGMA, RHOL, L, CP
  PRINT COMMENT & NUCLEATION THEORY QUANTITIES$
 PRINT RESULTS RAD, NDOT, DELG, G
RINITIALIZE FOR NOZZLE COMPUTATIONS STARTING AT THE CONDENS-
```



```
RATION POINT. THE VECTOR X CONTAINS THE POINTS ALONG THE
 RAXIS OF THE NOZZLE AT WHICH THE QUANTITIES DESIRED ARE TO
 REE COMPUTED. NOTE THAT IT IS NOT NECESSARY THAT THE SPACING
 RBE UNIFORM SINCE A VECTOR DELX IS PROVIDED. AT EACH POINT
 ROF THE MESH WE WANT TO CALCULATE
       P = VAPOR PRESSURE
 R
     RHO = MIXTURE DENSITY
 R
      T = TEMPERATURE
 R
       U = FLOW VELOCITY
      M = MACH NUMBER
  DELG = CONDENSATE INCREASE SINCE THE LAST MESH POINT
      G = FRACTION, BY MASS, OF THE VAPOR THAT IS IN THE
           CONDENSED STATE
RDELR(I) = THE INCREASE IN RADIUS, SINCE THE LAST POINT, OF
           THE DROPS INITIALLY FORMED AT POINT I
R RAD(I) = RADIUS OF DROPS INITIALLY FORMED AT X(I)
RNDOT(I) = THE NUMBER OF DROPS PER SECOND THAT ARE NEWLY
          FORMED FROM X(I-1) TO X(I)
  SIGMA = SURFACE TENSION
   RHOL = LIQUID DENSITY
      CP = SPECIFIC HEAT AT CONSTANT PRESSURE
 R
       L = LATENT HEAT
 RALSO THE IDENTIFYING QUANTITIES
 R = POINT OF EVALUATION
    DELX = DISTANCE FROM LAST MESH POINT
 R A = NOZZLE AREA
R DELA = AREA INCREASE FROM LAST MESH POINT
RONLY THE POINTS, THEIR INCREMENTS AND THE INTEGER INDEX N RARE KEPT IN CORE, ALL THE REST OF THE INFORMATION IS MAIN-
 RTAINED ON TAPE. ALL QUANTITIES FOR POINT N, HOWEVER, ARE
 RREQUIRED TO OBTAIN THOSE FOR POINT N+1, HENCE THEY ARE
RTEMPORARILY IN CORE AS UNINDEXED QUANTITIES WITH THE ABOVE
 RNAMES.
      INITIALIZE TO CONDENSATION POINT
Ř
 T=TCON
 P=PCON
 RHO=RHOCON
 U=UCON
 M=MCON
 X = X \subset ON
 A=ACON
 EXECUTE NOZZLE. ($AREA$, XCON-DELX, A(1))
 DELA=A-A(1)
 N=0
PPOINT=0
 EXECUTE IOCTRL.
                         DELU= .0001 * UCON
 XLIMIT=XCON+XRANGE
R
R
 U(1)=U+DELU
    WHENEVER U(1) . L.O.
    PRINT COMMENT $4 THE INITIAL APPROXIMATION TO THE VELO
 1CITY AT THE NEXT MESH POINT IS NEGATIVE.$
     TRÂNSFER TO $34
    END OF CONDITIONAL
```



```
BEGIN ITERATION ON DELG UNTIL NUCLEATION THEORY AND
          R
                 FLOW EQUATIONS AGREE. A MAXIMUM OF GITER ITERATIONS ARE
          R
                 ALLOWED PER MESH POINT.
530
           ITER=GITER
           N=N+1
               WHENEVER N.G.1000
               PRINT COMMENT $4
                                     NUMBER OF MESH POINTS EXCEEDS THE PRO
           1GRAMMED LIMIT.5
               TRANSFER TO $34
               END OF CONDITIONAL
           DELX(N)=DELX
            X(N) = X(N-1) + DELX(N)
               WHENEVER X.G.XLIMIT
               PRINT COMMENT $4
                                    THE NEXT POINT WOULD EXCEED THE RANGE
           1 DESIRED.5
               TRANSFER TO $34
               END OF CONDITIONAL
            EXECUTE NOZZLE . (SAREAS, X(N), A(1))
               WHENEVER A(1) .F .O .
                                    NOZZLE SUBROUTINE ERROR INDICATION -
               PRINT COMMENT $4
           1MESH POINT DOES NOT LIE INSIDE NOZZLE.$
               PRINT RESULTS X(N)
               TRANSFER TO $34
               END OF CONDITIONAL
            DELA(1) = A(1) - A
           DELG(1) = DELG
            G(1) = G + DELG(1)
            EXECUTE CFLOW. (A(1), DELA(1), G(1), DELG(1), P, RHU, T, U, M)
531
            L=FL.(T(1))
            TDROP=C/(B-ELOG • (P(1)))
            RHOL = FRHOL . (TDROP)
            SIGMA = FSIGMA . (TDROP)
           TEST=G(1)
          EXECUTE NUCLE2. (X(N),DELX(N),A(1),DELA(1),P(1),RHO(1),T(1),
          1U(1),M(1),MDOT,ALPHA,N,RAD,DRAD,NDOT,DELG(1))
           G(1) = G + DELG(1)
            TEST=.ABS.(TEST-G(1))
            WHENEVER TEST.L. .00001 , TRANSFER TO 532
            ITER=ITER-1.
           WHENEVER ITER.GE.O., TRANSFER TO S31
            PRINT COMMENT $ .....$
532
           X = X(N)
           DELX=DFLX(N)
            A = A(1)
            DELA=DELA(1)
            P=P(1)
            RHO=RHO(1)
            T = T(1)
            DELU=U(1)-U
            U=U(1)
            M=M(1)
            DELG=DFLG(1)
            G=G(1)
            THROUGH S33, FOR I=0,1, I.G. (N-1)
            RAD(I) = RAD(I) + DRAD(I)
533
            EXECUTE IOCTRL.
          R
```



```
TRANSFER TO S29
 TRANSFER TO START
R
R
   INTERNAL FUNCTION FOR OUTPUT OF THE FLOW QUANTITIES AT
R MESH POINT X. LATER THIS SECTION MAY ALSO SAVE THIS
   INFORMATION FOR FURTHER PROCESSING.
 INTERNAL FUNCTION
 ENTRY TO IOCTRL.
 WHENEVER N.E.PPOINT
                     NOZZLE CONDITIONS -- $
 PRINT COMMENT $4
 PRINT RESULTS N, X, DELX, A, DELA, P, RHO, T, U, M, RAD(N), NDOT(N),
1DELG,G
     WHENEVER N.G.O
 PRINT RESULTS RAD(0) . . . RAD(N-1)
    END OF CONDITIONAL
PPOINT=N+XPOINT
 END OF CONDITIONAL
FUNCTION RETURN
END OF FUNCTION
R
 INTEGER I, N, PPOINT
 DIMENSION DELX(1000), DRAD(1000), NDOT(1000), RAD(1000), X(1000)
 DIMENSION A(1), DELA(1), DELG(1), G(1), M(1), P(1), RHO(1), T(1),
1 \cup (1), Z(1)
 VECTOR VALUES XPOINT = 1
 VECTOR VALUES LITER = 10.
```

VECTOR VALUES GITER = 10.

END OF PROGRAM

534



EXP=.5*(GAMMA+1.)*EXP



Z=2.*Z/(GAMMA+1.)
Z=(Z .P. EXP)/A2
A1=ASTAR*Z
R
FUNCTION RETURN
R
END OF FUNCTION



```
&COMPILE MAD, PRINT OBJECT, PUNCH OBJECT
                                                               CFLOW001CFLOW00*
                       AERONAUTICAL ENGINEERING
          R
                     NOZZLE CONDENSATION RESEARCH
          R
          R
                           CONDENSATION FLOW
          RRESEARCH-- J. GRIFFIN PROGRAMMING-- L. HARDING JULY 1963
          RCOMPUTATION OF VALUES OF PRESSURE, DENSITY, TEMPERATURE, MACH
          RNUMBER AND VFLOCITY THAT SATISFY THE FLOW EQUATIONS THAT
          RAPPLY AFTER THE ONSET OF CONDENSATION. IT IS ASSUMED THAT WE
          RHAVE COMPUTED THE CONDITIONS AT X AND DESIRE THOSE AT X+DELX
          RTHE ARGUMENTS REQUIRED ARE
             DELA = AREA INCREASE FROM X TO X+DELX
                A = AREA AT X+DELX
          R
             DELG = CONDENSATE MASS INCREASE FROM X TO X+DELX
          R
                G = CONDENSATE MASS AT X+DELX
          R
                P = PRESSURE AT X
             RHC = DENSITY AT X
                T = TEMPERATURE AT X
                U = VELOCITY AT X
          R
                M = MACH NUMBER AT X
          RTHE PARAMETERS CP, L AND MU ARE REQUIRED FROM PROGRAM COMMON.
          RTHE FUNCTION FL. (T) MUST BE USED HOWEVER SINCE ITERATION ON
          RT IS NECESSARY. THE UNKNOWN QUANTITIES ARE RETURNED IN P(1),
          RRHO(1), T(1), U(1) AND M(1). IT IS ASSUMED THAT U(1) CONTAINS
          RAN INITIAL APPROXIMATION TO THE VELOCITY AT THE NEXT MESH
          RPOINT ON ENTRY.
          EXTERNAL FUNCTION (A,DELA,G,DELG,PA,RHOA,TA,UA,MA)
          PROGRAM COMMON GAMMA, MU, B, C, CP, L, RHOL, SIGMA
          ENTRY TO CFLOW.
          U=UA(1)
          DELU=U-UA
          MDQG=DELG/(1 - G)
           DQA=DELA/A
          L=FL.(TA)
          R
          THROUGH S2, FOR I=1,1,1.G.100
          DQU=DELU/U
          Ŕ
               COMPUTATION OF DELT AND T FROM THE ENERGY EQUATION
          DELT=(L*DELG-U*DELU)/CP
          T=TA+DFLT
          L=FL \cdot (T)
               COMPUTE DELRHO/RHO FROM CONTINUITY EQUATION
          DQRHO=DQA+DQU
          DORHO = - DORHO
                COMPUTE DELP/P FROM THE EQUATION OF STATE
          R
          DOP=DORHO+(DELT/1)-MDQG
```

TWE CAN NOW COMPUTE THE VELOCITY CORRESPONDING TO



R THESE DIFFERENCE QUOTIENTS FROM THE MOMENTUM EQUATION R
DELU=-(DQP*R*T*(1G))/(MU*U) NEWU=UA+DELU
TEST=•ABS•(1•-NEWU/U)
U=NEWU
WHENEVER TEST.L.EPSLON, TRANSFER TO S3
R
R ITERATION LIMIT HAS BEEN REACHED WITHOUT CONVERGENCE R
PRINT COMMENT \$ 'CFLOW' - ITERATION FAILED TO CONVERGES EXECUTE ERROR.
R
R CONVERGENCE CRITERIA SATISFIED
R
TA(1)=T UA(1)=U
DQRHO=1 • -DQRHO
DQP=1DQP
PA(1)=PA/DQP
RHOA(1)=RHOA/DQRHO
NEWT=R*GAMMA*T/MU
MA(1)=U/SQRT.(NEWT)
FUNCTION RETURN
R
VECTOR VALUES R=8.314E+07
VECTOR VALUES EPSLON=1.E-06
INTEGER I
END OF FUNCTION



```
SCUMPILE MAD, PRINT OBJECT, PUNCH OBJECT
                                                                 NUCL1001NUCL100*
          R
                        AERONAUTICAL ENGINEERING
          R
                      NOZZLE CONDENSATION RESEARCH
          R
          R
                          NUCLEATION THEORY - 1
          RRESEARCH-- J. GRIFFIN PRUGRAMMING-- L. HARDING
                                                                JULY 1963
          RCOMPUTATION OF THE MASS DUE TO INITIAL CONDENSATION AS GIVEN
          RBY NUCLEATION THEORY. THE FOLLOWING QUANTITIES MUST BE AVAIL-
          RABLE.
          R(1) CONSTANTS
                NA = AVOGADROS NUMBER (MOLECULES/GRAM MOLE)
                 K = BOLTZMANN CONSTANT (DYNE*CM/DEGREEK)
                 R = UNIVERSAL GAS CONSTANT (DYNE*CM/GRAM MOLE*DEGREEK)
          R(2) PARAMETERS
          R
                  B = SATURATION CURVE CONSTANT
          R
                  C = SATURATION CURVE CONSTANT
                DELX = DELTA X FOR VOLUME
          R
               MDOT = RHOSAT*ASAT*USAT
                MU = MOLECULAR WEIGHT OF VAPOR
          R
          R(3) VARIABLES
                  A = NOZZLE AREA
          R
                  P = PRESSURE
          R
                 T = TEMPERATURE
          R
               RHOL = LIQUID DENSITY DEPENDENT ON TEMPERATURE
              SIGMA = SURFACE TENSION DEPENDENT ON TEMPERATURE
          R
          EXTERNAL FUNCTION (A1, A2, A3, A4, A5, A6, A7, A8)
          PROGRAM COMMON GAMMA, MU, B, C, CP, L, RHOL, SIGMA
          R
          RCOMPUTE THE RADIUS OF THE DROPS CONDENSING UNDER THESE
          RCONDITIONS, THEIR NUMBER AND HENCE THE CONDENSATE MASS
          RFORMED IN A VOLUME ELEMENT OF LENGTH DELX. THE PROGRAM
          RCOMMON PARAMETERS RHOL AND SIGMA ARE ASSUMED TO CORRESPOND
          RTO THE DROP TEMPERATURE FOR THE GIVEN FLOW CONDITIONS.
          ENTRY TO NUCLE1.
          A = A 1
          DELX=A2
          MDOT = A3
           P=A4
           T = A5
          Ř
          R
                COMPUTE RADIUS ( CM. ) OF THE DROPS THAT ARE CONDENSING
          RADIUS=(2.*SIGMA*MU)/(RHOL*T)
          RADIUS=RADIUS/(R*(ELOG.(P)-B+C/T))
          R
         Ř.
                COMPUTE THE NUMBER OF DROPS OF THIS SIZE THAT ARE
                CONDENSING PER CENTIMETER CUBED PER SECOND.
          R
          TEXP=RADIUS*RADIUS/K
          TEXP = - (4.1887902*SIGMA*TEXP)/T
          N=SQRT.(SIGMA*MU/NA(1))
         N=P*N/(K(1)*T)
           N=P*N*EXP (TEXP)/(K*T*RHOL)
```

N= . 7978846*N



NDOT=N*A*DELX
R COMPUTATION OF PERCENT OF LIQUID MASS, DELTAG
DELG=4.1887902*RHOL*NDOT*RADIUS
DELG=DELG*RADIUS*RADIUS/MDOT
R
A6=RADIUS
A7=NDOT
A8=DELG
FUNCTION RETURN
R
VECTOR VALUES NA=6.027E+23,6.027E+03
VECTOR VALUES K=1.379E-16,1.379E-06
VECTOR VALUES R=8.314E+07
R
END OF FUNCTION



```
SCOMPILE MAD, PRINT OBJECT, PUNCH OBJECT
                                                                NUCL2001NUCL200*
                       AERONAUTICAL ENGINEERING
         R
                      NOZZLE CONDENSATION RESEARCH
         R
         R
                          NUCLEATION THEORY - 2
         R
         RRESEARCH-- J. GRIFFIN PROGRAMMING-- L. HARDING JULY 1963
         RCOMPUTATION OF THE QUANTITIES ARISING DUE TO CONDENSATION
         RUNDER THE FOLLOWING CONDITIONS
                X = NOZZLE COORDINATE
         R
             DELX = INCREMENT SINCE LAST MESH POINT
         Ŕ
                A = NOZZLE AREA AT X
         R
             DELA = NOZZLE AREA INCREASE SINCE X-DELX
         R
                P = PRESSURE AT X
         R
               RHO = MIXTURE DENSITY AT X
         R
                T = TEMPERATURE AT X
                U = VELOCITY OF FLOW AT X
         R
         R
                M = MACH NUMBER AT X
         R
             MDOT = TOTAL MASS FLOW RATE
         R
            ALPHA = ACCOMODATION COEFFICIENT
         R
                N = MESH POINT NUMBER SINCE CONDENSATION. THE POINT
                    OF CONDENSATION IS MESH POINT ZERO.
         RTHE QUANTITIES TO BE COMPUTED ARE
         R RAD(N) = RADIUS OF NEW DROPS FORMED AT X. ( RAD(I) IS RADIUS
         R
                    AT X-DELX OF DROPS INITIALLY FORMED AT MESH POINT
         Ŕ
                     I AND IS NECESSARY INPUT )
         RNDOT(N) = NUMBER OF DROPS OF RADIUS RAD(N) FORMED BETWEEN
         R
                    X-DELX AND X. ( NDOT(I) IS THE NUMBER OF DROPS
                    INITIALLY FORMED BETWEEN MESH POINTS I-1 AND I AND
         Ŕ
                    IS NECESSARY INPUT. )
         RDELR(0) = DELR(I) IS THE RADIUS INCREASE BETWEEN X-DELX AND X
                    OF THOSE DROPS INITIALLY FORMED BETWEEN MESH
         R THRU
         RDELR(N-1) POINTS I-1 AND I, THESE QUANTITIES MUST ALL BE
                    COMPUTED. )
         R
             DELG = CONDENSATE MASS INCREASE FROM X-DELX TO X DUE TO
         Ŕ
                    NEWLY FORMED DROPS AND GROWTH OF OLD DROPS.
         R
         RTHE ARGUMENTS ARE THE QUANTITIES GIVEN ABOVE IN THAT ORDER.
         RNOTE THAT THE ZEROTH WORD OF THE VECTOR ARGUMENTS ARE TO BE
         RGIVEN, FURTHER THESE VECTORS CONTAIN REQUIRED INPUT AS WELL
         RAS SPACE TO PUT THE DESIRED OUTPUT. FURTHER THE USUAL
         RPROGRAM COMMON PARAMETERS ARE ASSUMED TO CORRESPOND TO THE
         RARGUMENT TEMPERATURE.
          EXTERNAL FUNCTION (X,DELX,A,DELA,P,RHO,T,U,M,MDOT,ALPHA,N,
         1
           RAD DELR NDOT DELG
         R
          PROGRAM COMMON GAMMA, MU, B, C, CP, L, RHOL, SIGMA
          INTEGER N
          ENTRY TO NUCLE2.
          EXECUTE NUCLEI. (A,DELX,MDOT,P,T,RAD(N),NDOT(N),DELG)
         R
               WE HAVE NOW ONLY TO COMPUTE THE RADIAL INCREMENTS AND
         R
                THEIR CONTRIBUTION TO THE CONDENSATE MASS INCREASE. THE
         R
               DROP TEMPERATURE IS TAKEN AS THE SATURATION CURVE
         R
                TEMPERATURE CORRESPONDING TO THE GIVEN PRESSURE.
         R
```



```
TUROP=C/(B-ELOG.(P))
           DELR= 7978.846 * SQRT. ( 1.379*.6027/(T*MU)) * ( TDROP-T )
           DELR=DELX*(ALPHA/L)*(P/RHOL)*(DELR/U)
           THROUGH S1, FOR I=1,1, I.G. (N-1)
S 1
           DELR(I) = DELR
          R
                COMPUTATION OF RESULTANT TOTAL CONDENSATE MASS INCREASE
          R
          DELG2=0.
           THROUGH S2, FOR I=0,1, I.G. (N-1)
S 2
           DELG2=DELG2+ RAD(I)*RAD(I)*NDOT(I)*DELR(I)
          DELG=DELG+12.5663706*RHOL*DELG2/MDOT
          R
           FUNCTION RETURN
           INTEGER I
           END OF FUNCTION
```



```
SCOMPILE MAD, PRINT OBJECT, PUNCH OBJECT
                                                                 NOZLEOO1NUZLEOO*
          R
                        AERONAUTICAL ENGINEERING
          R
                      NOZZLE CONDENSATION RESEARCH
          R
          R
                                 NOZZLE
          RRESEARCH-- J. GRIFFIN PROGRAMMING-- L. HARDING
                                                                JULY 1963
          RORIGIN OF THE COORDINATE SYSTEM FOR THE NOZZLE IS THE CENTER
          ROF THE THROAT, I.E., A(0) = ASTAR. THE VARIABLE X INCREASES
          RPOSITIVELY IN THE DIRECTION OF FLOW AND IS NEGATIVE UPSTREAM
          REFROM THE THROAT. THE NOZZLE PARAMETERS ARE
                ASTAR = THROAT AREA
                 XMIN = X-COORDINATE OF INTAKE
          R
                 xMAX = x-COORDINATE OF EXIT
                      = INTAKE HALF ANGLE IN DEGREES
                INANG
                OUTAMG = EXIT SIDE HALF ANGLE IN DEGREES
          RIHE ENTRY THROAT READS AND PRINTS THESE PARAMETERS.
           EXTERNAL FUNCTION (A1, A2, A3)
           ENTRY TO NOZZLE.
                     WHENEVER A1 .E. STHROATS
          R
               RETURN THROAT AREA AND INITIALIZE IF NECCESSARY
           READ DATA
           PRINT COMMENT $0
                                     NOZZI F PARAMETERS$
           PRINT RESULTS ASTAR, INANG, OUTANG
           PRINT RESULTS XMIN, XMAX
           A=INANG/RADIAN
           INTAN=SIN.(A)/COS.(A)
           A=OUTANG/RADIAN
           OUTTAN=SIN.(A)/COS.(A)
          A3=ASTAR
           FUNCTION RETURN
          R
                     OR WHENEVER A1 . E. SAREAS
          R
                COMPUTE THE AREA AT A2 AND RETURN IN A3
           WHENEVER (XMIN.L.A2) .AND. (A2.L.O.)
           A=INTAN*(.ABS. A2)
           OR WHENEVER (A2.G.O.) .AND. (A2.L.XMAX)
           SA*NATTUC=A
           OTHERWISE
           A3=0.
           WHENEVER A2.E.O., A3=ASTAR
           FUNCTION RETURN
           END OF CONDITIONAL
           A3=ASTAR+2.*A
           FUNCTION RETURN
          R
                     OR WHENEVER A1 .E. SINVERSS
          R
                COMPUTE THAT POINT ON THE X-AXIS OF THE NOZZLE THAT
          R
                HAS AREA 'A3'. THIS POINT DEPENDS ON THE MACH NUMBER
          R
                WHICH MUST BE IN A2 ON ENTRY, SEE THE PROGRAM FOR
          R
                THE PARTICULARS. IF A2(1) IS 1. ON RETURN THEN THE
          R
                SOLUTION IS IN A2, IF IT IS ZERO THEN THE SOLUTION IS
```



R STORED IN A2 BUT DOES NOT LIE INSIDE THE NOZZLE.
A=•5*(A3-ASTAR)
WHENEVER A.L.O., A=O.
X(1)=1.
MACH=A2
WHENEVER MACH.1.
X=-A/INTAN
WHENEVER XMIN.G.X,X(1)=0.
OTHERWISE
X=A/OUTTAN
WHENEVER X.G.XMAX,X(1)=0.
END OF CONDITIONAL
A2=X
A2(1)=X(1)
FUNCTION RETURN
R
END OF CONDITIONAL
R
INTEGER A1
DIMENSION X(1)
VECTOR VALUES RADIAN=57.2957795
R
END OF FUNCTION



\$COMPILE	MAD, PRINT OBJECT, PUNCH OBJECT	VAPOROO1VAPOROO*
	R AERONAUTICAL ENGINEERING	
	R NOZZLE CONDENSATION RESEARCH	
	R	
	R VAPOR PARAMETERS	
	R	
	RRESEARCH J. GRIFFIN PROGRAMMING L. HARDING R	JULY 1963
	RCOMPUTE AS A FUNCTION OF TEMPERATURE THE FUNCTIONS	
	R RHOL = LIQUID DENSITY	
	R L = LATENT HEAT	
	R SIGMA = SURFACE TENSION .	
	RNOTE THAT EACH OF THE QUANTITIES MAY BE COMPUTED SI	NGLY AND
	RTHAT THEIR VALUES ARE STORED IN LOW CORE. THIS PERM	IITS THEM
	RTO BE HELD CONSTANT WITHOUT INITIALIZING THESE SUBR	
	RANY ONE, OR ALL, OF THESE PARAMETERS MAY BE HELD CO	NSTANT BY
	RSIMPLY RETURNING THE VALUE FROM PROGRAM COMMON.	
	RIT IS TO BE NOTED THAT SIGMA AND RHOL ARE FUNCTIONS	OF THE
	RDROP TEMPERATURE, NOT THE VAPOR TEMPERATURE. IT IS	
	RTEMPERATURE THEN THAT MUST BE USED IN CALLING ON TH	
	RENTRIES, WHEREAS THE VAPOR TEMPERATURE IS USED WHEN RTHE LATENT HEAT.	COMPUTING
	R	
	EXTERNAL FUNCTION (T)	
	R	
	PROGRAM COMMON GAMMA, MU, B, C, CP, L, RHOL, SIGMA	
	R	
	ENTRY TO FRHOL.	
	R COMPUTE THE VALUE OF THE LIQUID DENSITY	
	FUNCTION RETURN VALUE	
	R	
	ENTRY TO FL.	AMERICAN AND THE SERVICE AND ADDRESS OF THE SERV
	R COMPUTE THE VALUE OF THE LATENT HEAT	
	FUNCTION RETURN VALUE	
	R FAITRY TO SOLOW	
	ENTRY TO FSIGMA.	
	R COMPUTE THE VALUE OF THE SURFACE TENSION	
	FUNCTION RETURN VALUE	WAS THE BROWN SAME WHILE AS NO. 114
	END OF FUNCTION	



APPENDIX C

INPUT DATA

- 1. Summary of input data and units required.
- 2. Table of input data used to obtain results plotted in Figures 1 through 13.
- 3. Plots of vapor properties obtained from References 20 through 24.



Summary of Input Data Requirements

Parameter	<u>Definition</u>	Units
PZERO	Initial pressure (P _O)	dyne/cm ²
RHZERO	Initial density (ρ_0)	gm/cm ³
TZERO	Initial temperature (T _O)	°K
PE	Initial approximation to saturation pressure (P _e)	dyne/cm ²
GAMMA	Ratio of specific heats (γ)	N. D.
MU	Molecular weight of the vapor (μ)	gm/gmol
CP	Specific heat (C _p)	dyne-cm/gm- ^o K
L	Latent heat (L)	dyne-cm/gm
SIGMA	Surface tension (σ)	dyne/cm
RHOL	Liquid density $(ho_L^{})$	gm/cm ³
C B	Saturation curve constants	gm/cm ³ {dyne/cm ² and ^O K
ALPHA	Accommodation coefficient (α)	N. D .
DELX	Incremental step in $X (\Delta x)$	cm
XRANGE	Length of interval, starting with condensation point, over which flow conditions will be computed	cm
XPOINT	Points which will be printed out, i.e., every fifth, tenth, etc., point.	N. D.
TRANGE	Temperature range over which program will search for condensation point	°K
DELTAT	Initial step size in condensation point search over TRANGE	°K
PERCNT	Value of epsilon for determination of onset of condensation	fraction
ASTAR	Throat area (A*)	cm ²
XMIN	X-coordinate of intake	cm
XMAX	X-coordinate of exit	cm
INANG	Inlet half angle	degrees



Summary of Input Data Requirements (continued)

OUTANG	Diffuser half angle $(\theta_{1/2})$	degrees
NA	Avogadro's number (in program) 6.027 x 10 ²³	molecules/gmol
R	Universal gas constant (in program) 8.314×10^7	dyne-cm/gmol ⁰ K
K	Boltzmann's constant (in program) 1. 379 x 10-16	dyne-cm/ ^O K



Table C-1. Input Data

	N ₂ (I)	N ₂ (II)	Cu	Zn(I)	Zn(II)
Po	8. 45 x 10 ⁶	8. 45 x 10 ⁶	1×10^6	1 x 10 ⁶	1 x 10 ⁶
$\rho_{_{\mathrm{O}}}$.00952	. 00961	2.54×10^{-4}	3.93×10^{-4}	6.04×10^{-4}
To	298	295	3000	1500	1300
Pe	2000	2000	166.7	166.7	166.7
γ	1.4	1.4	1.667	1.667	1.667
μ	28.02	28.02	63.54	65.37	65.37
C _p	1. 07 x 10^{7}	1.07×10^{7}		3.18×10^6	3.18×10^6
L	2. 3×10^9	2.3 x 10 ⁹	4.94×10^{10}	1.82×10^{10}	1.82 x 10 ¹⁰
σ	25. 8 22T	24. 25 22T	1300	1000 26 T	1000 26T
$ ho_{ m L}$	1.17700476 T	1.17700476 T	8.90007 T	7.40008T	7.40008T
C	882	882	34, 200	13,800	13,800
В	25.7	25. 7	25. 46	25. 3	25. 3
α	1.0	1.0	1.0	1.0	1.0
A*	. 0645	. 0645	. 645	. 645	. 645
Xmin	-5	-5	- 5	∞ 5	-5
Xmax	25	25	58	21.1	58
INANG	45	45	45	45	45
OUTANG	9.75	9.75	20	45	20



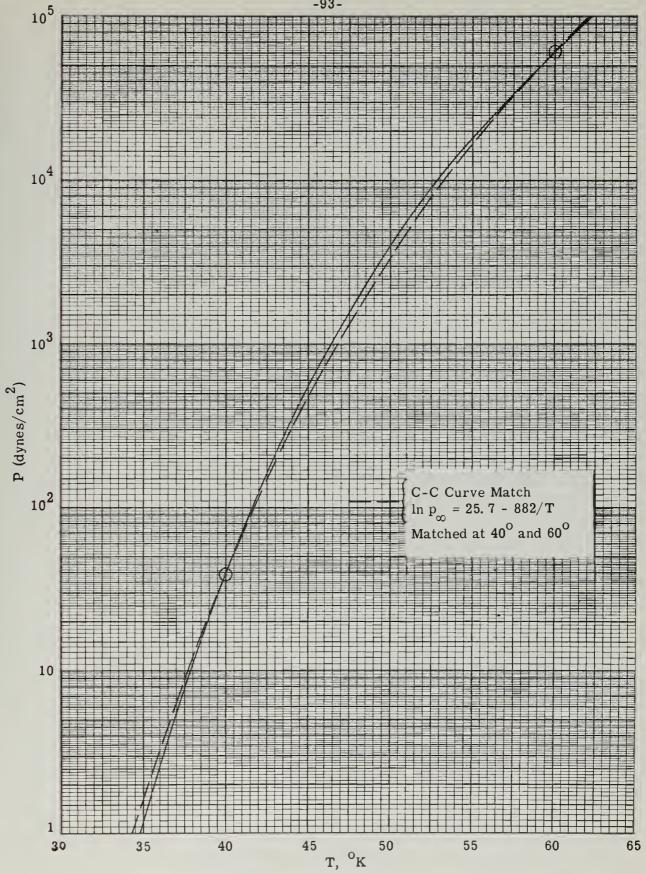


Figure C-1. Vapor Pressure of Nitrogen, NBS Circular 564 (24)



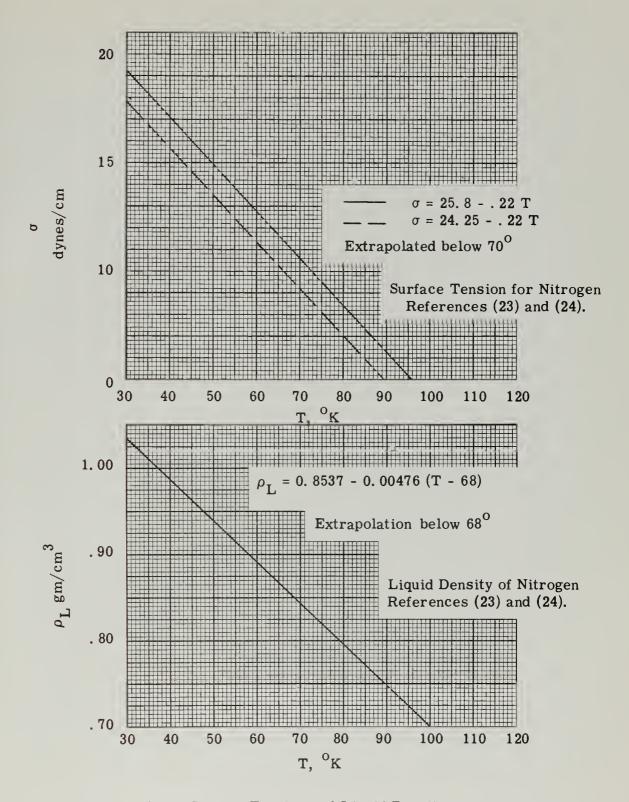


Figure C-2. Surface Tension and Liquid Density versus

Temperature for Nitrogen



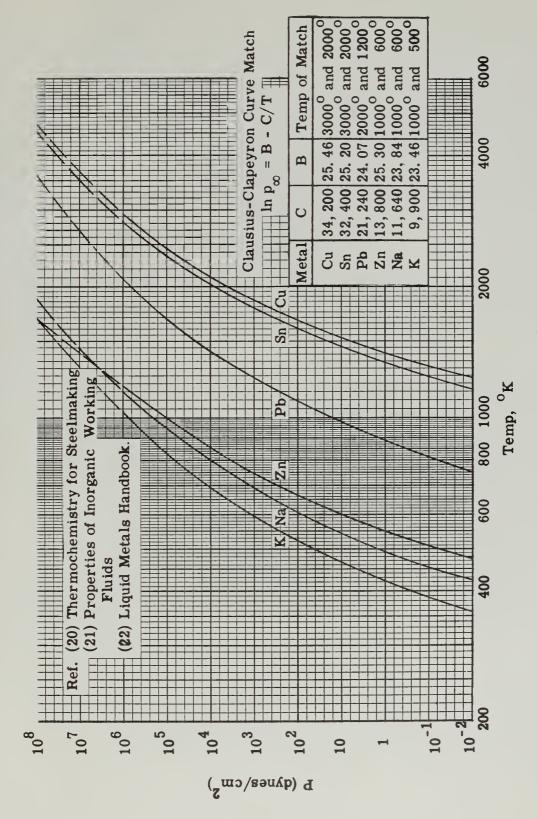


Figure C-3. Vapor Pressure Curves



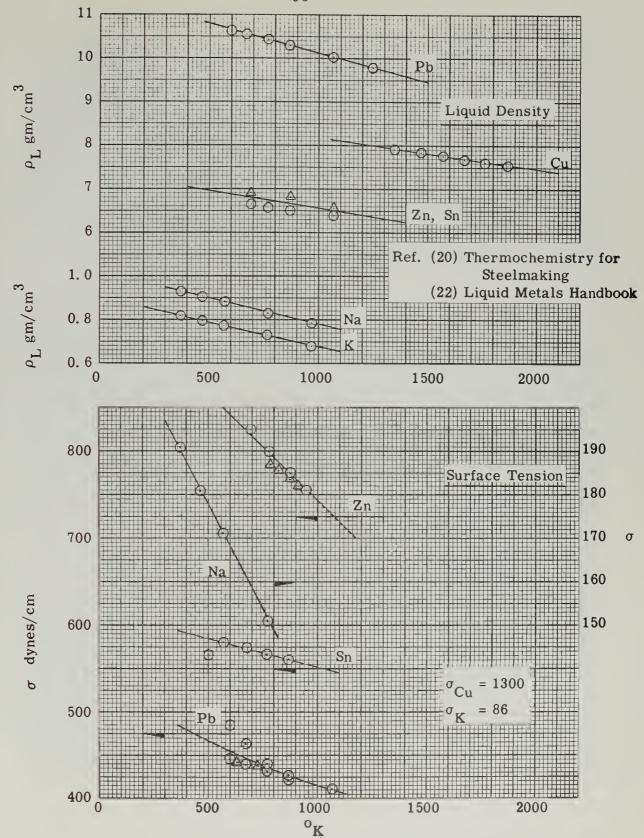
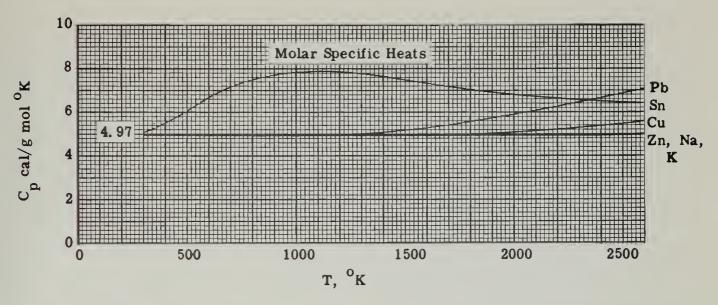


Figure C-4. Metal Vapor Properties





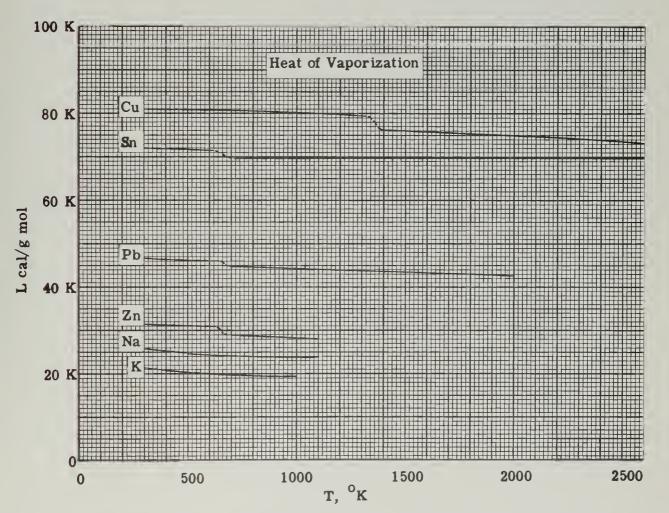


Figure C-5. Metal Vapor Properties from Thermochemistry for Steelmaking (20).

















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